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(54) **PREPARATION OF BOTTLEBRUSH
 POLYMERS VIA RING-OPENING
 METATHESIS POLYMERIZATION**

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C08F 8/02 (2006.01)
C08F 8/10 (2006.01)
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CPC ... **C08F 8/02** (2013.01); **C08F 8/10** (2013.01);
C08F 10/06 (2013.01); **C08G 61/08** (2013.01);
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2261/3324 (2013.01); **C08G 2261/418**
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(58) **Field of Classification Search**

CPC **C08F 10/06**; **C08F 8/02**; **C08F 8/10**;
C08F 2810/30; **C08G 61/08**; **C08G 2810/40**;
C08G 2261/1428; **C08G 2261/3324**; **C08G**
2261/418

See application file for complete search history.

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(Continued)

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(57) **ABSTRACT**

This invention relates to a reaction product obtained by ring-opening metathesis polymerization of norbornene ketones functionalized with the residual portion of a vinyl terminated macromonomer.

20 Claims, 4 Drawing Sheets

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Figure 1

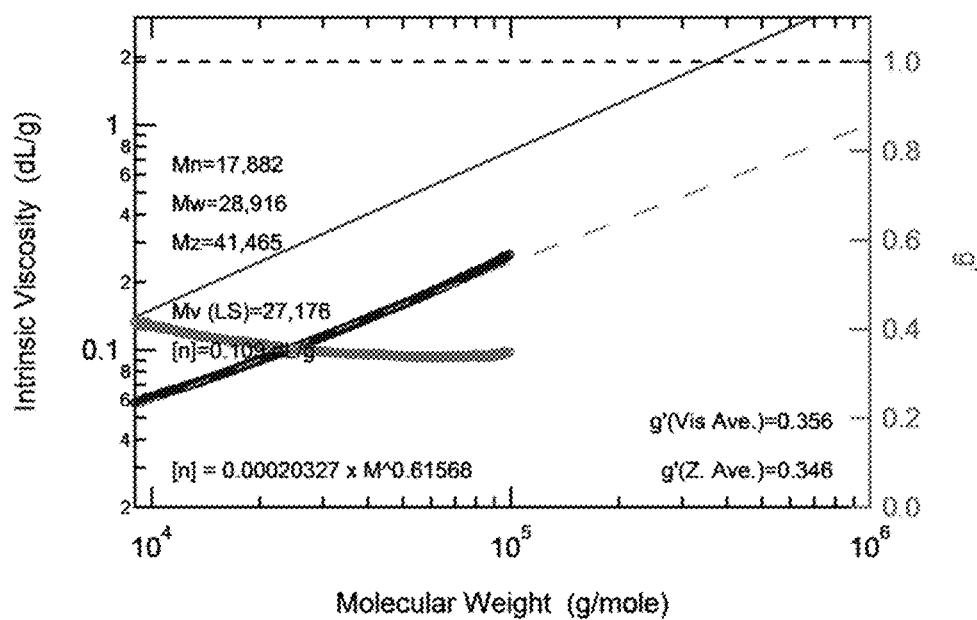
Intrinsic Viscosity vs. Molecular Weight by MALLS/3D Analysis.

Figure 2

Intrinsic Viscosity vs. Molecular Weight by MALLS/3D Analysis.

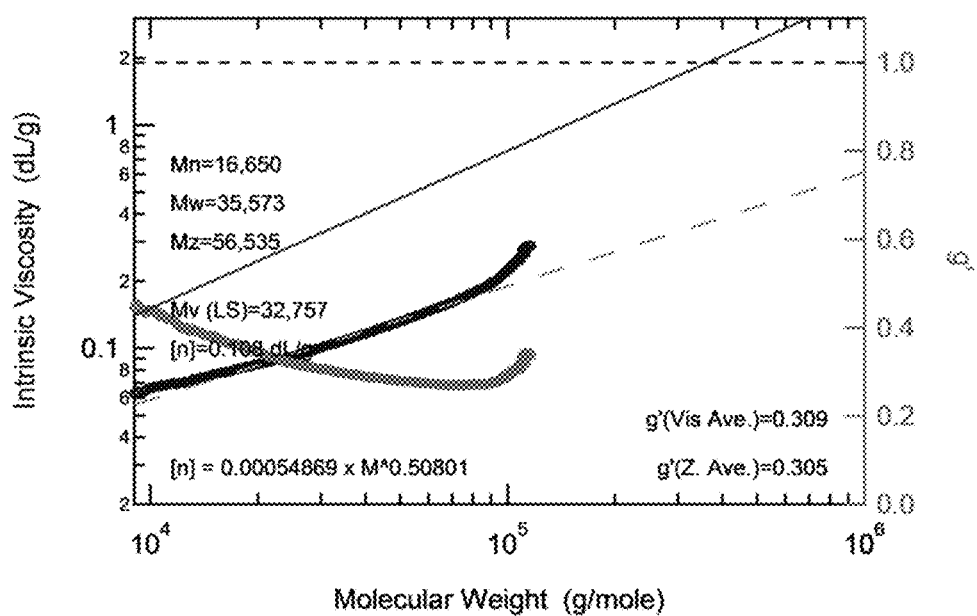


Figure 3

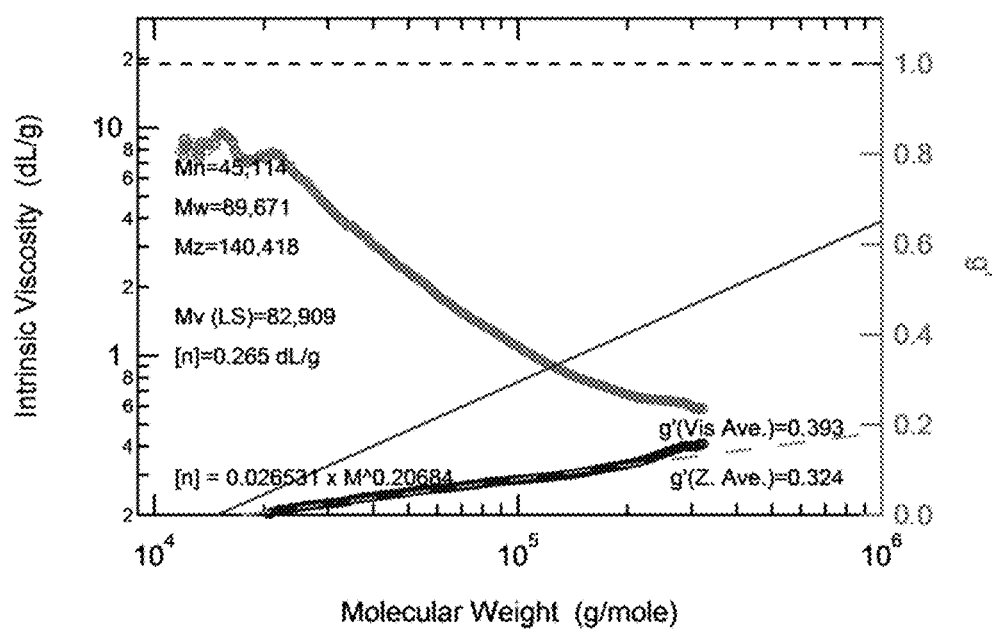
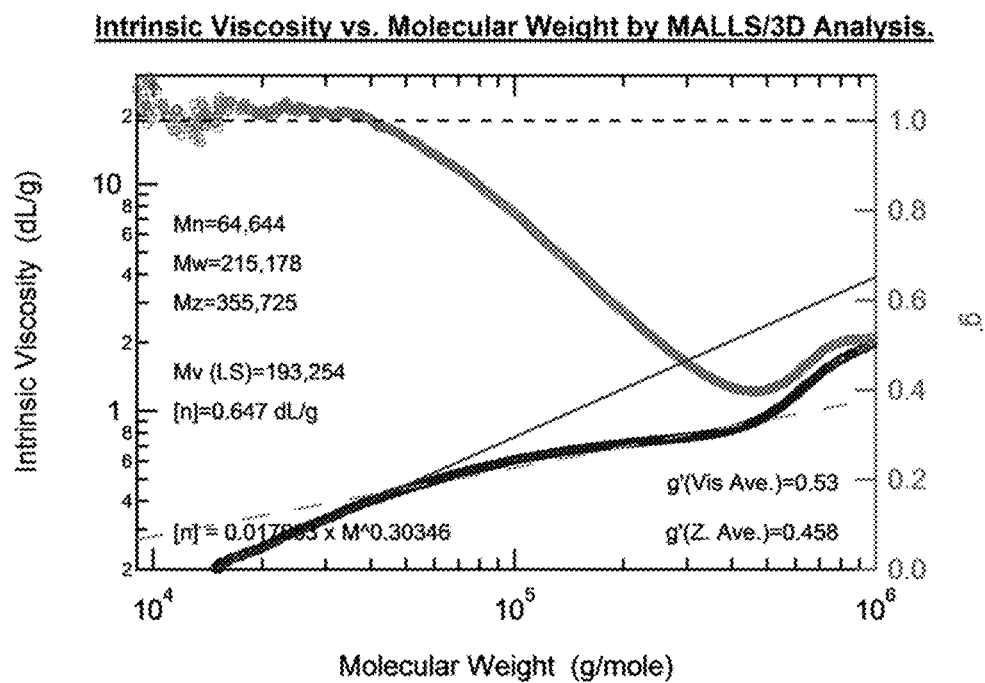
Intrinsic Viscosity vs. Molecular Weight by MALLS/3D Analysis.

Figure 4



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PREPARATION OF BOTTLEBRUSH POLYMERS VIA RING-OPENING METATHESIS POLYMERIZATION

PRIORITY CLAIM

This application claims priority to and the benefit of U.S. Provisional Application No. 61/758,535, filed Jan. 30, 2013 and EP 13160933.1 filed Mar. 25, 2013.

FIELD OF THE INVENTION

This invention relates to the preparation of highly-branched bottlebrush polymers derived from vinyl-terminated polymers via ring-opening metathesis polymerization.

BACKGROUND OF THE INVENTION

Metathesis is generally thought of as the interchange of radicals between two compounds during a chemical reaction. There are several varieties of metathesis reactions, such as ring opening metathesis, acyclic diene metathesis, ring closing metathesis, and cross metathesis. These reactions, however, have had limited success with the metathesis of functionalized olefins.

Methods for the production of polyolefins with end-functionalized groups are typically multi-step processes that often create unwanted by-products and waste of reactants and energy.

R. T. Mathers and G. W. Coates *Chem. Commun.*, 2004, pp. 422-423 disclose examples of using cross-metathesis to functionalize polyolefins containing pendant vinyl groups to form polar-functionalized products with a graft-type structure.

D. Astruc et al. *J. Am. Chem. Soc.* 2008, 130, pp. 1495-1506, and D. Astruc et al. *Angew. Chem. Int. Ed.*, 2005, 44, pp. 7399-7404 disclose examples of using cross metathesis to functionalize non-polymeric molecules containing vinyl groups.

For reviews of methods to form end-functionalized polyolefins, see: (a) S. B. Amin and T. J. Marks, *Angew. Chem. Int. Ed.*, 2008, 47, pp. 2006-2025; (b) T. C. Chung *Prog. Polym. Sci.*, 2002, 27, pp. 39-85; and (c) R. G. Lopez, F. D'Agosto, C. Boisson *Prog. Polym. Sci.*, 2007, 32, pp. 419-454.

U.S. Ser. No. 12/487,739, filed Jun. 19, 2009 discloses certain vinyl terminated oligomers and polymers that are functionalized, optionally, for use in lubricant applications.

U.S. Ser. No. 12/143,663, filed on Jun. 20, 2008 discloses certain vinyl terminated oligomers and polymers that are functionalized in U.S. Ser. No. 12/487,739, filed Jun. 19, 2009. U.S. Pat. No. 8,283,428 and U.S. Ser. No. 13/629,323, filed Sep. 27, 2012, which are incorporated by reference herein, provide polymacromonomers useful for functionalization.

U.S. Ser. No. 12/488,093, filed Jun. 19, 2009 discloses end functionalized polyolefins prepared from vinyl terminated polyolefins by cross metathesis.

Additional references of interest include U.S. Pat. Nos. 4,988,764; 6,225,432; 6,111,027; 7,183,359; 6,100,224; 5,616,153; PCT Publication Nos. WO 03/025084; WO 03/025038; WO 03/025037; WO 03/025036; WO 99/016845 and Amelia M. Anderson-Wilfe et al., "Synthesis and Ring-Opening Metathesis Polymerization of Norbornene-Terminated Syndiotactic Polypropylene", *Macromolecules*, 2012, 45 (19), pp. 7863-7877, published (web) Sep. 19, 2012.

Thus, metathesis reactions can provide functionalized polyolefins that have end-functionalization. However, to date

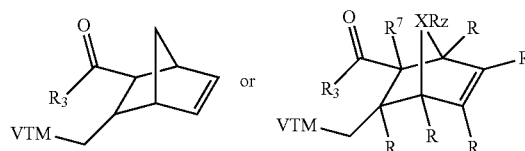
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it has not been feasible to polymerize polyolefins having end-functionalization to each other.

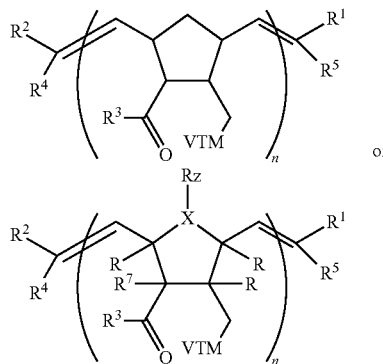
Thus, a need exists for a method to prepare polyolefins that utilize end-functionalization to provide new polymers with unique physical properties.

SUMMARY OF THE INVENTION

This invention relates to the reaction product obtained by contacting: 1) a metathesis catalyst, and 2) a C2 to a C40 vinyl or vinylen containing monomer, with 3) a composition represented by the formula:



where VTM is the residual terminal portion of a vinyl terminated macromonomer and R^3 is a C1 to a C40 hydrocarbyl group, each R is, independently, H or a C1 to C40 hydrocarbyl group and R^7 is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl, X is C or a heteroatom (such as N, O, S, or P) and z is 0 or 1. In one aspect, the reaction product can be characterized as a composition having the formula:



wherein VTM is the residual terminal portion of a vinyl terminated macromonomer;

each R^1 , R^2 , R^4 and R^5 , independently, a C2 to C40 hydrocarbyl group, (such as a residual portion of a vinyl C2 to a C40 monomer or vinylidene C3 to a C40 monomer);

R^3 is a C1 to a C40 hydrocarbyl group;

each R is, independently, H or a C1 to C40 hydrocarbyl group;

R^7 is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl;

X is C or a heteroatom (such as N, O, S, or P);

z is 0 or 1; and

n is from 2 to about 2000.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 provides intrinsic viscosity versus molecular weight of Example 10 product measured by MALLS/3D analysis.

FIG. 2 provides intrinsic viscosity versus molecular weight of Example 11 product measured by MALLS/3D analysis.

FIG. 3 provides intrinsic viscosity versus molecular weight of Example 12 product measured by MALLS/3D analysis.

FIG. 4 provides intrinsic viscosity versus molecular weight of Example 13 product measured by MALLS/3D analysis.

DEFINITIONS

In the structures depicted throughout this specification and the claims, a solid line indicates a bond, and an arrow indicates that the bond may be dative.

As used herein, the new notation for the Periodic Table Groups is used as described in *Chemical and Engineering News*, 63(5), p. 27 (1985).

The term “substituted” means that a hydrogen group has been replaced with a hydrocarbyl group, a heteroatom, or a heteroatom containing group. For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group and ethyl alcohol is an ethyl group substituted with an —OH group.

The terms “hydrocarbyl radical,” “hydrocarbyl,” and “hydrocarbyl group” are used interchangeably throughout this document. Likewise, the terms “functional group,” “group,” and “substituent” are also used interchangeably in this document. For purposes of this disclosure, “hydrocarbyl radical” is defined to be radicals of carbon and hydrogen, that may be linear, branched, or cyclic (aromatic or non-aromatic); and may include substituted hydrocarbyl radicals as defined herein. In an embodiment, a functional group may comprise a hydrocarbyl radical, a substituted hydrocarbyl radical, or a combination thereof.

Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been substituted with a heteroatom or heteroatom containing group, or with atoms from Groups 13, 14, 15, 16, and 17 of the Periodic Table of Elements, or a combination thereof, or with at least one functional group, such as halogen (Cl, Br, I, F), NR*, OR*, SeR*, TeR*, PR*, AsR*, SbR*, SR*, BR*, SiR*, GeR*, SnR*, PbR*, and the like or where at least one heteroatom has been inserted within the hydrocarbyl radical, such as halogen (Cl, Br, I, F), O, S, Se, Te, NR*, PR*, AsR*, SbR*, BR*, SiR*, GeR*, SnR*, PbR*, and the like, where R* is, independently, hydrogen or a hydrocarbyl radical, or any combination thereof.

In an embodiment, the hydrocarbyl radical is independently selected from methyl, ethyl, ethenyl, and isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl, triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, and triacontynyl. Also included are isomers of saturated, partially unsaturated, and aromatic cyclic structures wherein the radical may additionally be subjected to the types of substitutions described above. Examples include phenyl, methylphenyl, benzyl, methylbenzyl, naphthyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and the like. For this disclosure, when a radical is

listed, it indicates that radical type and all other radicals formed when that radical type is subjected to the substitutions defined above. Alkyl, alkenyl, and alkynyl radicals listed include all isomers including, where appropriate, cyclic isomers, for example, butyl includes n-butyl, 2-methylpropyl, 1-methylpropyl, tert-butyl, and cyclobutyl (and analogous substituted cyclopropyls); pentyl includes n-pentyl, cyclopentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and neopentyl (analogous substituted cyclobutyls and cyclopropyls); and butenyl includes E and Z forms of 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-1-propenyl, and 2-methyl-2-propenyl (cyclobutenyls and cyclopropenyls). Cyclic compounds having substitutions include all isomer forms, for example, methylphenyl would include ortho-methylphenyl, meta-methylphenyl, and para-methylphenyl; dimethylphenyl would include 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-diphenylmethyl, 3,4-dimethylphenyl, and 3,5-dimethylphenyl.

An “olefin,” alternatively referred to as “alkene,” is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, including, but not limited to, ethylene, propylene, and butene, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an “ethylene” content of 35 wt % to 55 wt %, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt % to 55 wt %, based upon the weight of the copolymer. A “polymer” has two or more of the same or different mer units. A “homopolymer” is a polymer having mer units that are the same. A “copolymer” is a polymer having two or more mer units that are different from each other. A “terpolymer” is a polymer having three mer units that are different from each other. “Different” as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An oligomer is a polymer having a low molecular weight. In some embodiments, an oligomer has an Mn of 21,000 g/mol or less (e.g., 2,500 g/mol or less); in other embodiments, an oligomer has a low number of mer units (such as 75 mer units or less).

An “alpha-olefin” is an olefin having a double bond at the alpha (or 1-) position. A “linear alpha-olefin” or “LAO” is an olefin with a double bond at the alpha position and a linear hydrocarbon chain. A “polyalphaolefin” or “PAO” is a polymer having two or more alpha-olefin units. For the purposes of this disclosure, the term “α-olefin” includes C₂-C₂₀ olefins. Non-limiting examples of α-olefins include ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, 1-nonacosene, 1-triacontene, 4-methyl-1-pentene, 3-methyl-1-pentene, 5-methyl-1-nonene, 3,5,5-trimethyl-1-hexene, vinylcyclohexane, and vinylnorbornane. Non-limiting examples of cyclic olefins and diolefins include cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene, norbornene, 4-methylnorbornene, 2-methylcyclopentene, 4-methylcyclopentene, vinylcyclohexane, norbornadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, vinylcyclohexene, 5-vinyl-

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2-norbornene, 1,3-divinylcyclopentane, 1,2-divinylcyclohexane, 1,3-divinylcyclohexane, 1,4-divinylcyclohexane, 1,5-divinylcyclooctane, 1-allyl-4-vinylcyclohexane, 1,4-diallylcyclohexane, 1-allyl-5-vinylcyclooctane, and 1,5-diallylcyclooctane.

For purposes herein, a polymer or polymeric chain comprises a concatenation of carbon atoms bonded to each other in a linear or a branched chain, which is referred to herein as the backbone of the polymer (e.g., polyethylene). The polymeric chain may further comprise various pendent groups attached to the polymer backbone which were present on the monomers from which the polymer was produced. These pendent groups are not to be confused with branching of the polymer backbone, the difference between pendent side chains and both short and long chain branching being readily understood by one of skill in the art.

The terms "catalyst" and "catalyst compound" are defined to mean a compound capable of initiating catalysis. In the description herein, the catalyst may be described as a catalyst precursor, a pre-catalyst compound, or a transition metal compound (for example, a metallocene compound), and these terms are used interchangeably. A catalyst compound may be used by itself to initiate catalysis or may be used in combination with an activator to initiate catalysis. When the catalyst compound is combined with an activator to initiate catalysis, the catalyst compound is often referred to as a pre-catalyst or catalyst precursor. A "catalyst system" is a combination of at least one catalyst compound, an optional activator, an optional co-activator, and an optional support material, where the system can polymerize monomers to polymer. For the purposes of this invention and the claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

An "anionic ligand" is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. A "neutral donor ligand" is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion.

A "scavenger" is a compound that is typically added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments, a co-activator can be pre-mixed with the catalyst compound to form an alkylated catalyst compound, also referred to as an alkylated invention compound.

A propylene polymer is a polymer having at least 50 mol % of propylene. As used herein, Mn is number average molecular weight as determined by proton nuclear magnetic resonance spectroscopy (^1H NMR) where the data is collected at 120° C. in a 5 mm probe using a spectrometer with a ^1H frequency of at least 400 MHz. Data is recorded using a maximum pulse width of 45°, 8 seconds between pulses and signal averaging 120 transients. Unless stated otherwise, Mw is weight average molecular weight as determined by gel permeation chromatography (GPC), Mz is z average molecular weight as determined by GPC as described in the VINYL TERMINATED MACROMONOMERS section below, wt % is weight percent, and mol % is mole percent. Molecular weight distribution (MWD) is defined to be Mw (GPC) divided by Mn (GPC). Unless otherwise noted, all molecular weight units, e.g., Mw, Mn, Mz, are g/mol.

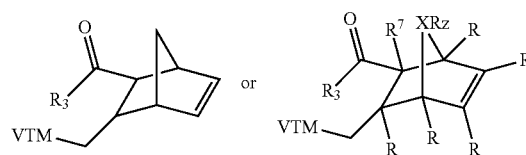
The following abbreviations may be used through this specification: Me is methyl, Ph is phenyl, Et is ethyl, Pr is propyl, iPr is isopropyl, n-Pr is normal propyl, Bu is butyl, iBu

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is isobutyl, tBu is tertiary butyl, p-tBu is para-tertiary butyl, nBu is normal butyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOAL is triisobutyl n-octylaluminum, MAO is methylalumoxane, pMe is para-methyl, Ar* is 2,6-diisopropylaryl, Bz is benzyl, THF is tetrahydrofuran, RT is room temperature which is defined as 25° C. unless otherwise specified, VTM is vinyl terminated macromonomer, and tol is toluene.

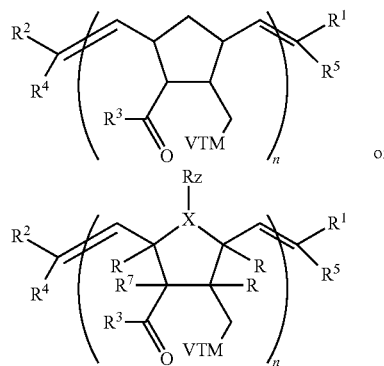
DETAILED DESCRIPTION OF THE INVENTION

This inventions relates to the reaction product obtained by contacting a by contacting a metathesis catalyst and a C2 to a C40 vinyl or vinylenes containing monomer with a composition represented by the formula:



where VTM is the residual terminal portion of a vinyl terminated macromonomer and R³ is a C1 to a C40 hydrocarbyl group, each R is, independently, H or a C1 to C40 hydrocarbyl group (preferably a substituted or unsubstituted alkyl or substituted or unsubstituted aryl) and R⁷ is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl, X is C or a heteroatom (such as N, O, S, or P) and z is 0 or 1.

In one aspect, the reaction product can be characterized as a composition represented by the formula



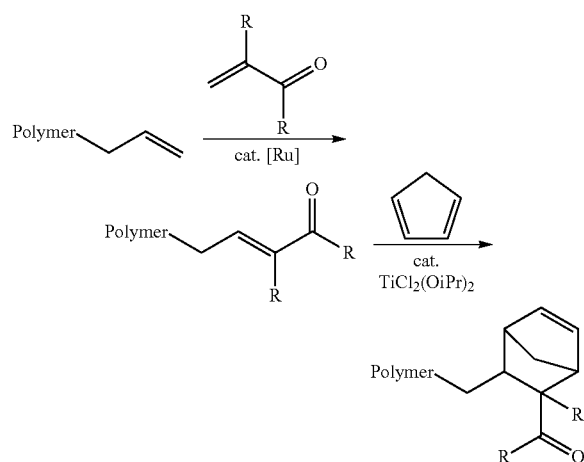
wherein VTM is the residual terminal portion of a vinyl terminated macromonomer; each R¹, R², R⁴ and R⁵, independently, a C2 to C40 hydrocarbyl group, (such as a residual portion of a vinyl C2 to a C40 monomer or vinylidene C3 to a C40 monomer); R³ is a C1 to a C40 hydrocarbyl group; each R is, independently, H or a C1 to C40 hydrocarbyl group; R⁷ is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl; X is C or a heteroatom (such as N, O, S, or P); z is 0 or 1; and n is from 2 to about 2000.

Process to Functionalize Monomers and Polymers

Olefin cross metathesis with a VTM, vinyl or vinylidene monomer and an alkyl en-one, preferably catalyzed by a

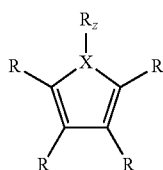
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ruthenium metathesis catalyst, outlined below, provides access to polar-functionalized VTMs, polar-functionalized vinyl monomers or polar-functionalized vinylidene monomers (noted as Polymer in the scheme below), which are then converted into norbornene-terminated polymers using a Diels Alder reaction, typically with a Ti catalyst and a cyclopentadiene or substituted cyclopentadiene. Notably, $\text{TiCl}_2(\text{OiPr})_2$ provides a balance of reactivity, maximizing conversion while minimizing byproduct formation.



where Polymer is a vinyl monomer (such as n-C16), a vinylidene monomer, or a VTM (such as an atactic homopolypropylene VTM, preferably an aPP having an M_n from 570 to 20,000, alternately from 3700 to 20,000 g/mol), each R is independently H, an alkyl (substituted or unsubstituted) or an aryl (substituted or unsubstituted) group, and Cat. Ru is a ruthenium metathesis catalyst.

Useful substituted cyclopentadienes include those substituted at one, two, three or more positions with the same or different C1 to C12 alkyl group (preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof), a heteroatom (preferably N, S, O, or P), or heteroatom containing group (preferably an N, O, S, or P containing group, preferably represented by the formula XR_n , where X is a heteroatom (preferably N, S, O, or P), R is H or a C1 to C12 alkyl, and n is 1 or 2, preferably the C1 to C12 alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof). Useful cyclopentadienes also include those where one carbon in the C5 ring has been replaced by a heteroatom (preferably N, O or S), such as substituted or unsubstituted furans, pyrroles, and the like. Useful cyclopentadienes include those represented by the formula (3):

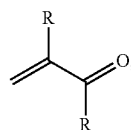


where z is 0 or 1, X is carbon or a heteroatom (preferably C, N, S, O or P, preferably C, O, S or N, preferably C, N or S); each R is, independently, H or a C1 to C12 alkyl group (preferably an alkyl selected from methyl, ethyl, propyl,

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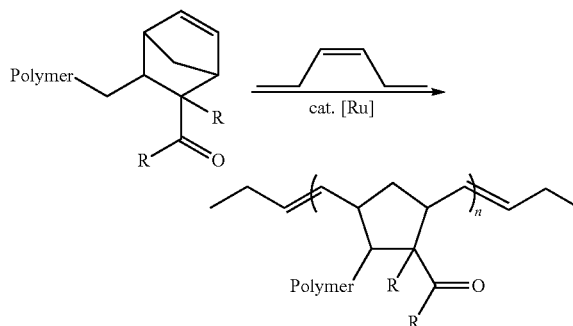
butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, and isomers thereof), or R may be XR_n , (where X is a heteroatom (such as N, O, S, or P), R is H or a C1 to C12 alkyl, and n is 1 or 2, preferably the C1 to C12 alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof).

Useful alkyl-en-ones include alkyl-en-ones where the alkyl has from 3 to 12 carbon atoms (preferably propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof), such as but-3-en-2-one, prop-2-en-one, pent-4-en-one, hex-5-en-one, oct-7-en-one, non-8-en-one, dec-9-en-one, undec-9-en-one, dodec-9-en-one and the like. Preferred alkyl en-ones are represented by the formula:



where each R is independently H, an alkyl (substituted or unsubstituted) or an aryl (substituted or unsubstituted) group, preferably the substituted or unsubstituted alkyl group has from 1 to 40 carbon atoms, preferably from 2 to 20 carbon atoms, preferably the alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof, and preferably the substituted or unsubstituted aryl group has from 5 to 40 carbon atoms, preferably from 6 to 20 carbon atoms.

With the polar-functionalized VTMs, polar-functionalized vinyl monomers or polar-functionalized vinylidene monomers, ring-opening metathesis polymerization (ROMP) is then performed using a metathesis catalyst (preferably a ruthenium-based catalyst), optionally in the presence of a chain transfer agent (such as 3-hexene), to control molecular weight. When these polymers are characterized by ^1H NMR and GPC 3D, the latter shows extensive branching, but, notabene, the linear viscosity standards used herein are based on polypropylene, not the exact polymer backbone.



Useful chain transfer agents include any C4 to C40 olefin (preferably having an internal or alpha double bond, preferably an internal double), such as 3-hexene, 2-butene, 2-hexene, 2-octene, 3-octene, 4-octene, 5-octene, 2-pentene, 3-pentene, and the like.

In an embodiment, this invention also relates to the reaction product obtained by contacting a cyclopentadiene (substituted or unsubstituted) with a titanium catalyst and an enone terminated VTM, vinyl, and or vinylidene monomer. Useful substituted cyclopentadienes include those substituted at one, two, three or more positions with the same or different C1 to

C12 alkyl group (preferably selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl, and isomers thereof), a heteroatom (preferably N, S, O, or P), or heteroatom containing group (preferably a N, O, S, or P containing group, preferably represented by the formula XR_n , where R is H or a C1 to C12 alkyl, and n is 1 or 2, preferably the C1 to C12 alkyl is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, and dodecyl, and isomers thereof). Useful cyclopentadienes also include those where one carbon in the C5 ring has been replaced by a heteroatom (preferably N, O or S), such as substituted or unsubstituted furans, pyrroles, and the like. Particularly useful cyclopentadienes include those represented by the formula (3) above. Useful enone terminated VTMs, enone terminated vinyl monomer, and/or enone terminated vinylidene monomer (also referred to as polar-functionalized VTMs, polar-functionalized vinyl monomers and/or polar-functionalized vinylidene monomer) include those having an Mw of about 100 to about 500,000 Daltons, preferably from about 100 to about 250,000 Da., preferably 500 to about 100,000 Da.

The reactants are typically combined in a reaction vessel at a temperature of 20° C. to 200° C. (preferably 50° C. to 160° C., preferably 60° C. to 140° C.) and a pressure of 0 to 1000 MPa (preferably 0.5 to 500 MPa, preferably 1 to 250 MPa) for a residence time of 0.5 seconds to 30 hours (preferably 1 second to 5 hours, preferably 1 minute to 1 hour).

Typically, in the first reaction to produce the polar functionalized VTMs, vinyl or vinylidene monomer, VTMs, vinyl monomer and/or vinylidene monomer are reacted with a cross metathesis catalyst and an alkyl-en-one. Typically, 0.00001 to 1.0 moles, preferably 0.0001 to 0.05 moles, preferably 0.0005 to 0.01 moles of metathesis catalyst are charged to the reactor per mole of monomer (e.g. one or more of vinyl monomer, VTMs, and vinylene monomer) charged and at least 1 mole of alkyl ene one is charged per mole of VTMs, preferably from 2:1 to 150:1, preferably from 5:1 to 100:1 moles of alkyl-en-one are charged to the reactor per mole of monomer (e.g. one or more of vinyl monomer, VTMs, and vinylene monomer) charged.

Typically, in the second reaction (to make norbornene containing polymer) polar-functionalized VTMs, polar-functionalized vinyl monomers and/or polar-functionalized vinylidene monomers are reacted with cyclopentadiene and a Ti catalyst. Typically 0.0001 to 2.0 moles, preferably 0.001 to 1.0 moles, preferably 0.04 to 0.5 moles of Ti catalyst are charged to the reactor per mole of polar-functionalized VTMs, polar-functionalized vinyl monomers and/or polar-functionalized vinylidene monomers charged and at least 1 mole of substituted or unsubstituted cyclopentadiene one is charged per mole of per mole of polar-functionalized VTMs, polar-functionalized vinyl monomers and/or polar-functionalized vinylidene monomers charged, preferably from 2:1 to 150:1, preferably 4:1 to 100:1 moles of substituted or unsubstituted cyclopentadiene are charged to the reactor per mole of polar-functionalized VTMs, polar-functionalized vinyl monomers and/or polar-functionalized vinylidene monomers charged.

Typically, in the third reaction, norbornene containing polymer is reacted with a metathesis catalyst, optionally in the presence of a chain transfer agent, and typically 0.0001 to 1.0 moles, preferably 0.001 to 0.05 moles, preferably 0.005 to 0.01 moles of metathesis catalyst are charged to the reactor per mole of norbornene containing polymer charged.

The process is typically a solution process, although it may be a bulk or high pressure process. Homogeneous processes are preferred. (A homogeneous process is defined to be a process where at least 90 wt % of the product is soluble in the

reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where reactant concentration in all feeds to the reactor is 70 vol % or more.) Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst or other additives, or amounts typically found with the reactants; e.g., propane in propylene).

Suitable diluents/solvents for the process include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof such as can be found commercially (Isopar™); perhalogenated hydrocarbons, such as perfluorinated C_{4-10} alkanes, chlorobenzene, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, mesitylene, and xylene. In a preferred embodiment, aliphatic hydrocarbon solvents are preferred, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In another embodiment, the solvent is not aromatic, preferably aromatics are present in the solvent at less than 1 wt %, preferably at 0.5 wt %, preferably at 0 wt % based upon the weight of the solvents.

In another embodiment, the process is a slurry process. As used herein the term "slurry polymerization process" means a polymerization process where a supported catalyst is employed and monomers are polymerized on the supported catalyst particles. At least 95 wt % of polymer products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

In a preferred embodiment, the feed concentration for the process is 60 vol % solvent or less, preferably 40 vol % or less, preferably 20 vol % or less.

The process may be batch, semi-batch or continuous. As used herein, the term continuous means a system that operates without interruption or cessation. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

Useful reaction vessels include reactors (including continuous stirred tank reactors, batch reactors, reactive extruder, pipe or pump).

This invention further relates to a process, preferably an in-line process, preferably a continuous process, to produce functionalized bottlebrush polymers.

A "reaction zone" also referred to as a "polymerization zone" is defined as an area where activated catalysts and monomers are contacted and a polymerization reaction takes place. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone. Room temperature is 23° C. unless otherwise noted.

Vinyl Terminated Macromonomers

A "vinyl terminated macromonomer," as used herein, refers to one or more of:

- (i) a vinyl terminated polymer having at least 5% allyl chain ends (preferably 15%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 98%, or 99%);
- (ii) a vinyl terminated polymer having an Mn of at least 160 g/mol, preferably at least 200 g/mol (measured by 1H

- NMR) comprising of one or more C₄ to C₄₀ higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends;
- (iii) a copolymer having an Mn of 300 g/mol or more (measured by ¹H NMR) comprising (a) from about 20 mol % to about 99.9 mol % of at least one C₅ to C₄₀ higher olefin, and (b) from about 0.1 mol % to about 80 mol % of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends;
- (iv) a copolymer having an Mn of 300 g/mol or more (measured by ¹H NMR), and comprises (a) from about 80 mol % to about 99.9 mol % of at least one C₄ olefin, (b) from about 0.1 mol % to about 20 mol % of propylene; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;
- (v) a co-oligomer having an Mn of 300 g/mol to 30,000 g/mol (measured by ¹H NMR) comprising 10 mol % to 90 mol % propylene and 10 mol % to 90 mol % of ethylene, wherein the oligomer has at least X % allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 * (\text{mol \% ethylene incorporated}) + 100)$, when 10 mol % to 60 mol % ethylene is present in the co-oligomer, 2) $X = 45$, when greater than 60 mol % and less than 70 mol % ethylene is present in the co-oligomer, and 3) $X = (1.83 * (\text{mol \% ethylene incorporated}) - 83)$, when 70 mol % to 90 mol % ethylene is present in the co-oligomer;
- (vi) a propylene oligomer, comprising more than 90 mol % propylene and less than 10 mol % ethylene wherein the oligomer has: at least 93% allyl chain ends, a number average molecular weight (Mn) of about 500 g/mol to about 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units;
- (vii) a propylene oligomer, comprising: at least 50 mol % propylene and from 10 mol % to 50 mol % ethylene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 20,000 g/mol, preferably 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol % to 3 mol %;
- (viii) a propylene oligomer, comprising: at least 50 mol % propylene, from 0.1 mol % to 45 mol % ethylene, and from 0.1 mol % to 5 mol % C₄ to C₁₂ olefin, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0;
- (ix) a propylene oligomer, comprising: at least 50 mol % propylene, from 0.1 mol % to 45 mol % ethylene, and from 0.1 mol % to 5 mol % diene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
- (x) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, an Mn of about 500 g/mol to about 70,000 g/mol, alternately to about 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
- (xi) vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(v_{ts})}$ of greater than 0.95; and (d) an Mn (¹H NMR) of at least 20,000 g/mol; and
- (xii) vinyl terminated polyethylene having: (a) at least 50%

(¹H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (¹H NMR) in the range of from about 0.8 to about 1.2.

It is understood by those of ordinary skill in the art that when the VTM's, as described here, are reacted with another material the "vinyl" (e.g. the allyl chain end) is involved in the reaction and has been transformed. Thus, the language used herein describing that a fragment of the final product (typically referred to as PO in the formulae herein) is the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon, is meant to refer to the fact that the VTM has been incorporated in the product. Similarly stating that a product or material comprises a VTM means that the reacted form of the VTM is present, unless the context clearly indicates otherwise (such as a mixture of ingredients that do not have a catalytic agent present).

In some embodiments, the vinyl terminated macromonomer has an Mn of at least 200 g/mol, (e.g., 200 g/mol to 100,000 g/mol, e.g., 200 g/mol to 75,000 g/mol, e.g., 200 g/mol to 60,000 g/mol, e.g., 300 g/mol to 60,000 g/mol, or e.g., 750 g/mol to 30,000 g/mol) (measured by ¹H NMR) and comprises one or more (e.g., two or more, three or more, four or more, and the like) C₄ to C₄₀ (e.g., C₄ to C₃₀, C₄ to C₂₀, or C₄ to C₁₂, e.g., butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof) olefin derived units, where the vinyl terminated macromonomer comprises substantially no propylene derived units (e.g., less than 0.1 wt % propylene, e.g., 0 wt %); and wherein the vinyl terminated macromonomer has at least 5% (at least 10%, at least 15%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%; at least 80%, at least 90%, or at least 95%) allyl chain ends (relative to total unsaturation); and optionally, an allyl chain end to vinylidene chain end ratio of 1:1 or greater (e.g., greater than 2:1, greater than 2.5:1, greater than 3:1, greater than 5:1, or greater than 10:1); and even further optionally, e.g., substantially no isobutyl chain ends (e.g., less than 0.1 wt % isobutyl chain ends). In some embodiments, the vinyl terminated macromonomers may also comprise ethylene derived units, e.g., at least 5 mol % ethylene (e.g., at least 15 mol % ethylene, e.g., at least 25 mol % ethylene, e.g., at least 35 mol % ethylene, e.g., at least 45 mol % ethylene, e.g., at least 60 mol % ethylene, e.g., at least 75 mol % ethylene, or e.g., at least 90 mol % ethylene). Such vinyl terminated macromonomers are further described in U.S. Ser. No. 13/072,288, which is hereby incorporated by reference.

In some embodiments, the vinyl terminated macromonomers may have an Mn (measured by ¹H NMR) of greater than 200 g/mol (e.g., 300 g/mol to 60,000 g/mol, 400 g/mol to 50,000 g/mol, 500 g/mol to 35,000 g/mol, 300 g/mol to 15,000 g/mol, 400 g/mol to 12,000 g/mol, or 750 g/mol to 10,000 g/mol), and comprise:

- (a) from about 20 mol % to 99.9 mol % (e.g., from about 25 mol % to about 90 mol %, from about 30 mol % to about 85 mol %, from about 35 mol % to about 80 mol %, from about 40 mol % to about 75 mol %, or from about 50 mol % to about 95 mol %) of at least one C₅ to C₄₀ (e.g., C₆ to C₂₀) higher olefin;
- (b) from about 0.1 mol % to 80 mol % (e.g., from about 5 mol % to 70 mol %, from about 10 mol % to about 65 mol %, from about 15 mol % to about 55 mol %, from about 25 mol % to about 50 mol %, or from about 30 mol % to about 80 mol %) of propylene; and

wherein the vinyl terminated macromonomer has at least 40% allyl chain ends (e.g., at least 50% allyl chain ends, at least 60% allyl chain ends, at least 70% allyl chain ends, or at least 80% allyl chain ends, at least 90% allyl chain ends, at least 95% allyl chain ends) relative to total unsaturation; and, optionally, an isobutyl chain end to allyl chain end ratio of less than 0.70:1, less than 0.65:1, less than 0.60:1, less than 0.50:1, or less than 0.25:1; and further optionally, an allyl chain end to vinylidene chain end ratio of greater than 2:1 (e.g., greater than 2.5:1, greater than 3:1, greater than 5:1, or greater than 10:1); and even further optionally, an allyl chain end to vinylene ratio is greater than 1:1 (e.g., greater than 2:1 or greater than 5:1). Such macromonomers are further described in U.S. Ser. No. 13/072,249, hereby incorporated by reference.

In another embodiment, the vinyl terminated macromonomer has an Mn of 300 g/mol or more (measured by ^1H NMR, e.g., 300 g/mol to 60,000 g/mol, 400 g/mol to 50,000 g/mol, 500 g/mol to 35,000 g/mol, 300 g/mol to 15,000 g/mol, 400 g/mol to 12,000 g/mol, or 750 g/mol to 10,000 g/mol), and comprises:

- (a) from about 80 mol % to about 99.9 mol % of at least one C_4 olefin, e.g., about 85 mol % to about 99.9 mol %, e.g., about 90 mol % to about 99.9 mol %;
- (b) from about 0.1 mol % to about 20 mol % of propylene, e.g., about 0.1 mol % to about 15 mol %, e.g., about 0.1 mol % to about 10 mol %; and

wherein the vinyl terminated macromonomer has at least 40% allyl chain ends (e.g., at least 50% allyl chain ends, at least 60% allyl chain ends, at least 70% allyl chain ends, or at least 80% allyl chain ends, at least 90% allyl chain ends, at least 95% allyl chain ends) relative to total unsaturation, and in some embodiments, an isobutyl chain end to allyl chain end ratio of less than 0.70:1, less than 0.65:1, less than 0.60:1, less than 0.50:1, or less than 0.25:1, and in further embodiments, an allyl chain end to vinylidene group ratio of more than 2:1, more than 2.5:1, more than 3:1, more than 5:1, or more than 10:1. Such macromonomers are also further described in U.S. Ser. No. 13/072,249, which is hereby incorporated by reference.

In other embodiments, the vinyl terminated macromonomer is a propylene co-oligomer having an Mn of 300 g/mol to 30,000 g/mol as measured by ^1H NMR (e.g., 400 g/mol to 20,000 g/mol, e.g., 500 g/mol to 15,000 g/mol, e.g., 600 g/mol to 12,000 g/mol, e.g., 800 g/mol to 10,000 g/mol, e.g., 900 g/mol to 8,000 g/mol, e.g., 900 g/mol to 7,000 g/mol), comprising 10 mol % to 90 mol % propylene (e.g., 15 mol % to 85 mol %, e.g., 20 mol % to 80 mol %, e.g., 30 mol % to 75 mol %, e.g., 50 mol % to 90 mol %) and 10 mol % to 90 mol % (e.g., 85 mol % to 15 mol %, e.g., 20 mol % to 80 mol %, e.g., 25 mol % to 70 mol %, e.g., 10 mol % to 50 mol %) of one or more alpha-olefin comonomers (e.g., ethylene, butene, hexene, or octene, e.g., ethylene), wherein the oligomer has at least X % allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 (\text{mol \% ethylene incorporated}) + 100) \{ \text{alternately } 1.20(-0.94 (\text{mol \% ethylene incorporated}) + 100), \text{ alternately } 1.50(-0.94 (\text{mol \% ethylene incorporated}) + 100) \}$, when 10 mol % to 60 mol % ethylene is present in the co-oligomer; 2) $X = 45$ (alternately 50, alternately 60), when greater than 60 mol % and less than 70 mol % ethylene is present in the co-oligomer; and 3) $X = (1.83 * (\text{mol \% ethylene incorporated}) - 83, \{ \text{alternately } 1.20 [1.83 * (\text{mol \% ethylene incorporated}) - 83], \text{ alternately } 1.50 [1.83 * (\text{mol \% ethylene incorporated}) - 83] \}$, when 70 mol % to 90 mol % ethylene is present in the co-oligomer. Such macromonomers are further described in U.S. Ser. No. 12/143,663, which is hereby incorporated by reference.

In other embodiments, the vinyl terminated macromonomer is a propylene oligomer, comprising more than 90 mol % propylene (e.g., 95 mol % to 99 mol %, e.g., 98 mol % to 9 mol %) and less than 10 mol % ethylene (e.g., 1 mol % to 4 mol %, e.g., 1 mol % to 2 mol %), wherein the oligomer has: at least 93% allyl chain ends (e.g., at least 95%, e.g., at least 97%, e.g., at least 98%); a number average molecular weight (Mn) of about 400 g/mol to about 30,000 g/mol, as measured by ^1H NMR (e.g., 500 g/mol to 20,000 g/mol, e.g., 600 g/mol to 15,000 g/mol, e.g., 700 g/mol to 10,000 g/mol, e.g., 800 g/mol to 9,000 g/mol, e.g., 900 g/mol to 8,000 g/mol, e.g., 1,000 g/mol to 6,000 g/mol); an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, and less than 1400 ppm aluminum, (e.g., less than 1200 ppm, e.g., less than 1000 ppm, e.g., less than 500 ppm, e.g., less than 100 ppm). Such macromonomers are further described in U.S. Ser. No. 12/143,663.

In other embodiments, the vinyl terminated macromonomer is a propylene oligomer, comprising: at least 50 mol % (e.g., 60 mol % to 90 mol %, e.g., 70 mol % to 90 mol %) propylene and from 10 mol % to 50 mol % (e.g., 10 mol % to 40 mol %, e.g., 10 mol % to 30 mol %) ethylene, wherein the oligomer has: at least 90% allyl chain ends (e.g., at least 91%, e.g., at least 93%, e.g., at least 95%, e.g., at least 98%); an Mn of about 150 g/mol to about 20,000 g/mol, as measured by ^1H NMR (e.g., 200 g/mol to 15,000 g/mol, e.g., 250 g/mol to 15,000 g/mol, e.g., 300 g/mol to 10,000 g/mol, e.g., 400 g/mol to 9,500 g/mol, e.g., 500 g/mol to 9,000 g/mol, e.g., 750 g/mol to 9,000 g/mol); and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.3:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol % to 3 mol % (e.g., at less than 1 mol %, e.g., less than 0.5 mol %, e.g., at 0 mol %). Such macromonomers are further described in U.S. Ser. No. 12/143,663.

In other embodiments, the vinyl terminated macromonomer is a propylene oligomer, comprising: at least 50 mol % (e.g., at least 60 mol %, e.g., 70 mol % to 99.5 mol %, e.g., 80 mol % to 99 mol %, e.g., 90 mol % to 98.5 mol %) propylene, from 0.1 mol % to 45 mol % (e.g., at least 35 mol %, e.g., 0.5 mol % to 30 mol %, e.g., 1 mol % to 20 mol %, e.g., 1.5 mol % to 10 mol %) ethylene, and from 0.1 mol % to 5 mol % (e.g., 0.5 mol % to 3 mol %, e.g., 0.5 mol % to 1 mol %) C_4 to C_{12} olefin (such as butene, hexene, or octene, e.g., butene), wherein the oligomer has: at least 90% allyl chain ends (e.g., at least 91%, e.g., at least 93%, e.g., at least 95%, e.g., at least 98%); a number average molecular weight (Mn) of about 150 g/mol to about 15,000 g/mol, as measured by ^1H NMR (e.g., 200 g/mol to 12,000 g/mol, e.g., 250 g/mol to 10,000 g/mol, e.g., 300 g/mol to 10,000 g/mol, e.g., 400 g/mol to 9500 g/mol, e.g., 500 g/mol to 9,000 g/mol, e.g., 750 g/mol to 9,000 g/mol); and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0. Such macromonomers are further described in U.S. Ser. No. 12/143,663.

In other embodiments, the vinyl terminated macromonomer is a propylene oligomer, comprising: at least 50 mol % (e.g., at least 60 mol %, e.g., 70 mol % to 99.5 mol %, e.g., 80 mol % to 99 mol %, e.g., 90 mol % to 98.5 mol %) propylene, from 0.1 mol % to 45 mol % (e.g., at least 35 mol %, e.g., 0.5 mol % to 30 mol %, e.g., 1 mol % to 20 mol %, e.g., 1.5 mol % to 10 mol %) ethylene, and from 0.1 mol % to 5 mol % (e.g., 0.5 mol % to 3 mol %, e.g., 0.5 mol % to 1 mol %) diene (such as C_4 to C_{12} alpha-omega dienes (such as butadiene, hexadiene, octadiene), norbornene, ethylidene norbornene, vinyl-norbornene, norbornadiene, and dicyclopentadiene), wherein the oligomer has at least 90% allyl chain ends (e.g., at least 91%, e.g., at least 93%, e.g., at least 95%, e.g., at least 98%); a number average molecular weight (Mn) of about 150 g/mol

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to about 20,000 g/mol, as measured by ^1H NMR (e.g., 200 g/mol to 15,000 g/mol, e.g., 250 g/mol to 12,000 g/mol, e.g., 300 g/mol to 10,000 g/mol, e.g., 400 g/mol to 9,500 g/mol, e.g., 500 g/mol to 9,000 g/mol, e.g., 750 g/mol to 9,000 g/mol); and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0. Such macromonomers are further described in U.S. Ser. No. 12/143,663.

In other embodiments, the vinyl terminated macromonomer is a propylene homo-oligomer, comprising propylene and less than 0.5 wt % comonomer, e.g., 0 wt % comonomer, wherein the oligomer has:

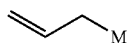
- i) at least 93% allyl chain ends (e.g., at least 95%, e.g., at least 96%, e.g., at least 97%, e.g., at least 98%, e.g., at least 99%);
- ii) a number average molecular weight (M_n) of about 500 g/mol to about 20,000 g/mol, as measured by ^1H NMR (e.g., 500 g/mol to 15,000 g/mol, e.g., 700 g/mol to 10,000 g/mol, e.g., 800 g/mol to 8,000 g/mol, e.g., 900 g/mol to 7,000 g/mol, e.g., 1,000 g/mol to 6,000 g/mol, e.g., 1,000 g/mol to 5,000 g/mol);
- iii) an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.3:1.0; and
- iv) less than 1400 ppm aluminum, (e.g., less than 1200 ppm, e.g., less than 1000 ppm, e.g., less than 500 ppm, e.g., less than 100 ppm). Such macromonomers are also further described in U.S. Ser. No. 12/143,663.

The vinyl terminated macromonomers may be homopolymers, copolymers, terpolymers, and so on. Any vinyl terminated macromonomers described herein has one or more of:

- (i) an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.3:1.0;
- (ii) an allyl chain end to vinylidene chain end ratio of greater than 2:1 (e.g., greater than 2.5:1, greater than 3:1, greater than 5:1, or greater than 10:1);
- (iii) an allyl chain end to vinylene ratio that is greater than 1:1 (e.g., greater than 2:1 or greater than 5:1); and
- (iv) at least 5% allyl chain ends (preferably at least 15%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 98%, or 99%) up to 100% allyl chain ends.

Vinyl terminated macromonomers generally have a saturated chain end (or terminus) and/or an unsaturated chain end or terminus. The unsaturated chain end of the vinyl terminated macromonomer comprises an "allyl chain end" or a "3-alkyl" chain end.

An allyl chain end is represented by $\text{CH}_2\text{CH}=\text{CH}_2$, as shown in the formula:

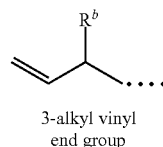


where M represents the polymer chain. "Allylic vinyl group," "allyl chain end," "vinyl chain end," "vinyl termination," "allylic vinyl group," and "vinyl terminated" are used interchangeably in the following description. The number of allyl chain ends, vinylidene chain ends, vinylene chain ends, and other unsaturated chain ends is determined using ^1H NMR at 120° C. using deuterated tetrachloroethane as the solvent on an at least 250 MHz NMR spectrometer, and in selected cases, confirmed by ^{13}C NMR. Resconi has reported proton and carbon assignments (neat perdeuterated tetrachloroethane used for proton spectra, while a 50:50 mixture of normal and perdeuterated tetrachloroethane was used for carbon spectra; all spectra were recorded at 100° C. on a BRUKER spectrometer operating at 500 MHz for proton and 125 MHz for carbon) for vinyl terminated oligomers in *J. American Chemical Soc.*, 114, 1992, pp. 1025-1032 that are useful

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herein. Allyl chain ends are reported as a molar percentage of the total number of moles of unsaturated groups (that is, the sum of allyl chain ends, vinylidene chain ends, vinylene chain ends, and the like).

A 3-alkyl chain end (where the alkyl is a C_1 to C_{38} alkyl), also referred to as a "3-alkyl vinyl end group" or a "3-alkyl vinyl termination," is represented by the formula:



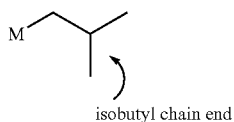
where "●●●●" represents the polyolefin chain and R^b is a C_1 to C_{38} alkyl group, or a C_1 to C_{20} alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. The amount of 3-alkyl chain ends is determined using ^{13}C NMR as set out below.

^{13}C NMR data is collected at 120° C. at a frequency of at least 100 MHz, using a BRUKER 400 MHz NMR spectrometer. A 90 degree pulse, an acquisition time adjusted to give a digital resolution between 0.1 and 0.12 Hz, at least a 10 second pulse acquisition delay time with continuous broadband proton decoupling using swept square wave modulation without gating is employed during the entire acquisition period. The spectra is acquired with time averaging to provide a signal to noise level adequate to measure the signals of interest. Samples are dissolved in tetrachloroethane- d_2 at concentrations between 10 wt % to 15 wt % prior to being inserted into the spectrometer magnet. Prior to data analysis spectra are referenced by setting the chemical shift of the TCE solvent signal to 74.39 ppm. Chain ends for quantization were identified using the signals shown in the table below. N-butyl and n-propyl were not reported due to their low abundance (less than 5%) relative to the chain ends shown in the table below.

Chain End	^{13}C NMR Chemical Shift
P~i-Bu	23.5 to 25.5 and 25.8 to 26.3 ppm
E~i-Bu	39.5 to 40.2 ppm
P~Vinyl	41.5 to 43 ppm
E~Vinyl	33.9 to 34.4 ppm

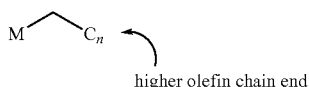
The "allyl chain end to vinylidene chain end ratio" is defined to be the ratio of the percentage of allyl chain ends to the percentage of vinylidene chain ends. The "allyl chain end to vinylene chain end ratio" is defined to be the ratio of the percentage of allyl chain ends to the percentage of vinylene chain ends. Vinyl terminated macromonomers typically also have a saturated chain end. In polymerizations where propylene is present, the polymer chain may initiate growth in a propylene monomer, thereby generating an isobutyl chain end. An "isobutyl chain end" is defined to be an end or terminus of a polymer, represented as shown in the formula below:

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where M represents the polymer chain. Isobutyl chain ends are determined according to the procedure set out in WO 2009/155471. The “isobutyl chain end to allylic vinyl group ratio” is defined to be the ratio of the percentage of isobutyl chain ends to the percentage of allyl chain ends. The “isobutyl chain end to alpha bromo carbon ratio” is defined to be the ratio of the percentage of isobutyl chain ends to the percentage of brominated chain ends (at about 34 ppm).

In polymerizations comprising C₄ or greater monomers (or “higher olefin” monomers), the saturated chain end may be a C₄ or greater (or “higher olefin”) chain end, as shown in the formula below:



where M represents the polymer chain and n is an integer selected from 4 to 40. This is especially true when there is substantially no ethylene or propylene in the polymerization. In an ethylene/(C₄ or greater monomer) copolymerization, the polymer chain may initiate growth in an ethylene monomer, thereby generating a saturated chain end which is an ethyl chain end.

Mn (¹H NMR) is determined according to the following NMR method. ¹H NMR data is collected at either room temperature or 120° C. (for purposes of the claims, 120° C. shall be used) in a 5 mm probe using a Varian spectrometer with a ¹H frequency of 250 MHz, 400 MHz, or 500 MHz (for the purpose of the claims, a proton frequency of 400 MHz is used). Data are recorded using a maximum pulse width of 45°, 8 seconds between pulses and signal averaging 120 transients. Spectral signals are integrated and the number of unsaturation types per 1000 carbons is calculated by multiplying the different groups by 1000 and dividing the result by the total number of carbons. Mn is calculated by dividing the total number of unsaturated species into 14,000, and has units of g/mol. The chemical shift regions for the olefin types are defined to be between the following spectral regions.

Unsaturation Type	Region (ppm)	Number of hydrogens per structure
Vinyl	4.95-5.10	2
Vinylidene (VYD)	4.70-4.84	2
Vinylene	5.31-5.55	2
Trisubstituted	5.11-5.30	1

Unless otherwise stated, Mn (GPC) is determined using the GPC-DRI method described below. Mn, Mw, and Mz may be measured by using a Gel Permeation Chromatography (GPC) method using a High Temperature Size Exclusion Chromatograph (SEC, either from Waters Corporation or Polymer Laboratories), equipped with a differential refractive index detector (DRI) and light scattering (LS) detector. Molecular weight distribution (MWD) is Mw (GPC)/Mn (GPC). Experimental details, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001) and references therein.

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Three Polymer Laboratories PLgel 10 mm Mixed-B columns are used. The nominal flow rate is 0.5 cm³/min and the nominal injection volume is 300 μL. The various transfer lines, columns and differential refractometer (the DRI detector) are contained in an oven maintained at 145° C. Solvent for the SEC experiment is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1,2,4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.7 μm glass pre-filter and subsequently through a 0.1 μm Teflon filter. The TCB is then degassed with an online degasser before entering the SEC. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160° C. with continuous agitation for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/mL at room temperature, 1.284 g/mL at 145° C., and 1.324 g/mL at 135° C. The injection concentration is from 0.5 to 2.0 mg/mL, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector and the injector are purged. Flow rate in the apparatus is then increased to 0.5 mL/minute, and the DRI is allowed to stabilize for 8 to 9 hours before injecting the first sample. The concentration, c, at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, I_{DRI}, using the following equation:

$$c = K_{DRI} I_{DRI} (dn/dc)$$

where K_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, n=1.500 for TCB at 135° C. and TCB at 145° C., and λ=690 nm. For purposes of this invention and the claims thereto, (dn/dc) is determined using GPC-DRI. Units of parameters used throughout this description of the SEC method are: concentration is expressed in g/cm³, molecular weight is expressed in g/mol, and intrinsic viscosity is expressed in dL/g.

The LS detector is a Wyatt Technology High Temperature DAWN HELEOS. The molecular weight, M, at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M. B. Hugglin, *LIGHT SCATTERING FROM POLYMER SOLUTIONS*, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{M P(\theta)} + 2A_2 c$$

Here, ΔR(θ) is the measured excess Rayleigh scattering intensity at scattering angle θ, c is the polymer concentration determined from the DRI analysis, A₂ is the second virial coefficient, and for purposes of this invention A₂=0.0006. P(θ) is the form factor for a monodisperse random coil, and K_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system determined by GPC-DRI. The refractive index, n=1.500 for TCB at 145° C. and λ=657 nm.

A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge

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configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c/[\eta] + 0.3(c[\eta])^2$$

where c is concentration and was determined from the DRI output.

The branching index (g'_{vis}) is calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

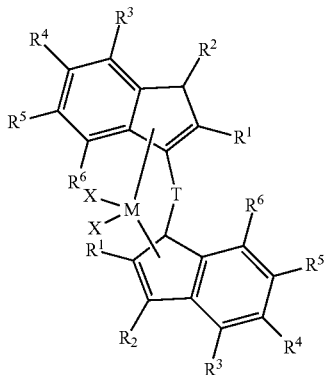
where the summations are over the chromatographic slices, i , between the integration limits.

The branching index g'_{vis} is defined as:

$$g'_{vis} = \frac{[\eta]_{avg}}{kM_v^\alpha}$$

where, for purpose of this invention and claims thereto $\alpha=0.705$ and $k=0.0002288$ for all polymers. M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. See Macromolecules, 2001, 34, pp. 6812-6820 and Macromolecules, 2005, 38, pp. 7181-7183, for guidance on selecting a linear standard having similar molecular weight and comonomer content, and determining k coefficients and α exponents.

In an embodiment, the product obtained herein is derived from a vinyl terminated propylene polymer. In an embodiment, the vinyl terminated propylene polymer is produced using a process comprising: contacting propylene, under polymerization conditions, with a catalyst system comprising an activator and at least one metallocene compound represented by the formula:



where:

M is hafnium or zirconium;

each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides,

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dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system);

each R^1 is, independently, a C_1 to C_{10} alkyl group;

each R^2 is, independently, a C_1 to C_{10} alkyl group;

each R^3 is hydrogen;

each R^4 , R^5 , and R^6 , is, independently, hydrogen or a substituted hydrocarbyl or unsubstituted hydrocarbyl group, or a heteroatom;

T is a bridging group;

further provided that any of adjacent R^4 , R^5 , and R^6 groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated; and

obtaining a propylene polymer having at least 50% allyl chain ends (relative to total unsaturations), as described in co-pending U.S. Ser. No. 13/072,280, filed Mar. 25, 2011, which is incorporated by reference in its entirety herein.

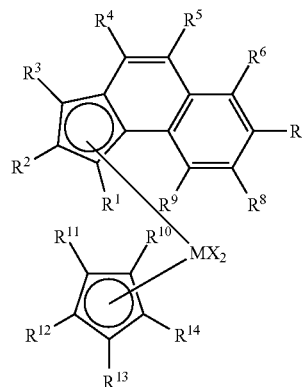
In an embodiment, the vinyl terminated propylene polymer is produced using a process comprising:

1) contacting:

a) one or more olefins with

b) a transition metal catalyst compound represented by the

formula:



wherein

M is hafnium or zirconium;

each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halogens, dienes, amines, phosphines, ethers, or a combination thereof;

each R^1 and R^3 are, independently, a C_1 to C_8 alkyl group; and each R^2 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are, independently, hydrogen, or a substituted or unsubstituted hydrocarbyl group having from 1 to 8 carbon atoms, provided however that at least three of the R^{10} - R^{14} groups are not hydrogen; and

2) obtaining vinyl terminated polymer having an Mn of 300 g/mol or more and at least 30% allyl chain ends (relative to total unsaturation), as described in co-pending U.S. Ser. No. 13/072,279, filed Mar. 25, 2011, which is incorporated by reference in its entirety herein.

In an embodiment, the polyolefin chain is derived from a higher olefin copolymer comprising allyl chain ends. In an embodiment, the higher olefin copolymer comprising allyl chain ends has an Mn of 300 g/mol or more (measured by 1H NMR) comprising:

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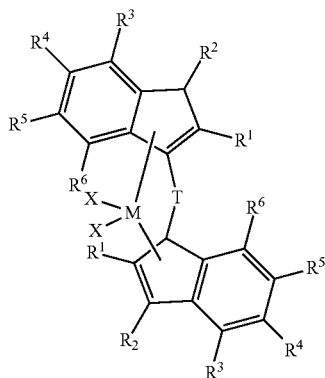
- (i) from about 20 mol % to about 99.9 mol % of at least one C₅ to C₄₀ higher olefin; and
 (ii) from about 0.1 mol % to about 80 mol % of propylene; wherein the higher olefin copolymer has at least 40% allyl chain ends, as described in U.S. Ser. No. 13/072,249, filed Mar. 25, 2011, which is incorporated by reference in its entirety herein.

In an embodiment, the product produced herein is derived from a vinyl terminated branched polyolefin. In an embodiment, the vinyl terminated branched polyolefin has an Mn (¹H NMR) of 7,500 to 60,000 g/mol, comprising one or more alpha olefin derived units comprising ethylene and/or propylene, and having;

- (i) 50% or greater allyl chain ends, relative to total number of unsaturated chain ends; and
 (ii) a g' _{vis} of 0.90 or less, as described in U.S. Ser. No. 61/467,681, filed Mar. 25, 2011, which is incorporated by reference in its entirety herein.

In an embodiment, the product produced herein is derived from a vinyl terminated branched polyolefin produced by a process for polymerization, comprising:

- (i) contacting, at a temperature greater than 35° C., one or more monomers comprising ethylene and/or propylene, with a catalyst system comprising a metallocene catalyst compound and an activator, wherein the metallocene catalyst compound is represented by the following formula:



where:

M is selected from the group consisting of zirconium or hafnium;

each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system);

each R¹, R², R³, R⁴, R⁵, and R⁶, is, independently, hydrogen or a substituted or unsubstituted hydrocarbyl group, a heteroatom or heteroatom containing group;

further provided that any two adjacent R groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated;

further provided that any of adjacent R⁴, R⁵, and R⁶ groups may form a fused ring or multicenter fused ring system where the rings may be aromatic, partially saturated or saturated;

T is a bridging group represented by the formula (Ra)₂J, where J is one or more of C, Si, Ge,

N or P, and each Ra is, independently, hydrogen, halogen, C₁ to C₂₀ hydrocarbyl or a C₁ to C₂₀ substituted hydrocarbyl,

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provided that at least one R³ is a substituted or unsubstituted phenyl group, if any of R¹, R², R⁴, R⁵, or R⁶ are not hydrogen;

- (ii) converting at least 50 mol % of the monomer to polyolefin; and

- (iii) obtaining a branched polyolefin having greater than 50% allyl chain ends, relative to total unsaturated chain ends and a Tm of 60° C. or more, as described in U.S. Ser. No. 61/467,681, filed Mar. 25, 2011, which is incorporated by reference in its entirety herein.

In an embodiment of the invention, the product produced herein is derived from a vinyl terminated ethylene polymer, preferably a vinyl terminated polyethylene (preferably in particulate form) having:

- (a) at least 60% allyl chain ends (preferably at least 65%, preferably at least 70%, preferably at least 75%, preferably at least 80%, preferably at least 85%, preferably at least 90%, preferably at least 95%, preferably at least 96%, preferably at least 97%, preferably at least 98%, preferably at least 99%, or preferably at least 100%);

- (b) a molecular weight distribution of less than or equal to 4.0 (preferably less than or equal to 3.8, preferably less than or equal to 3.5, preferably less than or equal to 3.2, preferably less than or equal to 3.0, preferably less than or equal to 2.8, or preferably less than or equal to 2.5);

- (c) an Mn (¹H NMR) of at least 20,000 g/mol (preferably at least 25,000 g/mol, preferably at least 30,000 g/mol, preferably at least 40,000 g/mol, preferably at least 50,000 g/mol, and, optionally, less than 125,000 g/mol, preferably less than 120,000, or preferably less than 110,000);

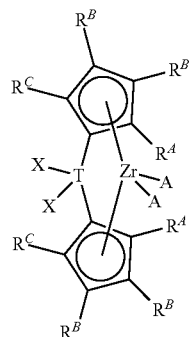
- (d) optionally, an Mn (GPC)/Mn (¹H NMR) in the range of from about 0.8 to about 1.2 (preferably from about 0.9 to about 1.1, preferably from about 0.95 to about 1.1); and

- (e) optionally, a g' _{vis} of greater than 0.95 (preferably greater than 0.96, preferably greater than 0.98, preferably greater than 0.98, and, optionally, preferably less than or equal to 1.0).

Preferably, the vinyl terminated ethylene polymers are prepared by a process comprising:

- (a) contacting ethylene with a supported metallocene catalyst system;

wherein the supported catalyst system comprises: (i) a support material; (ii) an activator having from about 1 wt % to about 14 wt % trimethylaluminum, based on the weight of the activator; and (iii) a metallocene compound represented by the formula:



wherein: T is Si or Ge; each R^A is a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl group; each R^B is, independently, H, or a C₁ to C₈ substituted or unsubstituted hydrocarbyl group, or a group represented by the formula —CH₂R^x; wherein R^x is a C₁ to C₂₀ substituted or unsubstituted hydro-

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carbyl group, provided that at least one R^B is methyl or a group represented by the formula $-\text{CH}_2\text{R}^x$; each R^C is, independently, H or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group; each A is independently selected from the group consisting of C_1 to C_{20} substituted or unsubstituted hydrocarbyl groups, hydrides, amides, amines, alkoxides, sulfides, phosphides, halides, dienes, phosphines, and ethers; each X is, independently, hydrogen, halogen or a C_1 to C_{20} hydrocarbyl, and two X groups can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system; further provided that any of adjacent R^A , R^B , and/or R^C groups may form a fused ring or multicenter fused ring systems, where the rings may be substituted or unsubstituted, and may be aromatic, partially unsaturated, or unsaturated;

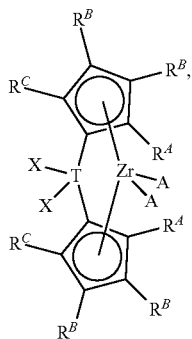
(b) obtaining a vinyl terminated polyethylene having: (i) at least 60% allyl chain ends; (ii) a molecular weight distribution of less than or equal to 4.0; and (iii) a Mn (^1H NMR) of at least 20,000 g/mol. Preferably, the vinyl terminated ethylene polymers are made according to the process (and using the catalyst systems) described in (U.S. Ser. No. 61/704,606, filed Sep. 24, 2012, entitled, Production of Vinyl Terminated Polyethylene Using Supported Catalyst System).

In an embodiment of the invention, the product produced herein is derived from a vinyl terminated ethylene polymer, preferably a vinyl terminated polyethylene having: (i) at least 50% allyl chain ends (preferably 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 100%); (ii) a molecular weight distribution of less than or equal to 4.0 (preferably less than or equal to 3.8, 3.6, 3.5, 3.4, 3.2, 3.0, 2.8, or 2.5); (iii) a $g'_{(vts)}$ of 0.95 or less (preferably less than 0.93, 0.90, 0.88, or 0.85); (iv) an Mn (^1H NMR) of at least 7,000 g/mol (preferably at least 10,000 g/mol, 15,000 g/mol, 20,000 g/mol, 25,000 g/mol, 30,000 g/mol, 45,000 g/mol, 55,000 g/mol, 65,000 g/mol, or 85,000 g/mol, and, optionally, less than 125,000 g/mol); and (v) a Mn (GPC)/Mn (^1H NMR) in the range of from about 0.8 to about 1.2 (preferably from 0.85 to 1.15, 0.90 to 1.10, and 0.95 to 1.00). Preferably, the vinyl terminated ethylene polymers are produced by a process comprising:

(a) contacting ethylene with a metallocene catalyst system; wherein the catalyst system comprises:

(i) an ionizing activator;

(ii) a metallocene compound represented by the formula:



wherein T is Si or Ge; each R^A is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group; each R^B is, independently, H or a C_1 to C_8 substituted or unsubstituted hydrocarbyl group, or a group represented by the formula $-\text{CH}_2\text{R}^x$; wherein R^x is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group, provided that at least one R^B is methyl or a group represented by the formula $-\text{CH}_2\text{R}^x$; each R^C is, inde-

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pendently, H or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group; each A is independently selected from the group consisting of C_1 to C_{20} substituted or unsubstituted hydrocarbyl groups, hydrides, amides, amines, alkoxides, sulfides, phosphides, halides, dienes, phosphines, and ethers; each X is, independently, hydrogen, halogen, or a C_1 to C_{20} hydrocarbyl, and two X groups can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system; further provided that any of adjacent R^A , R^B , and/or R^C groups may form a fused ring or multicenter fused ring systems, where the rings may be substituted or unsubstituted, and may be aromatic, partially unsaturated, or unsaturated;

(b) obtaining a vinyl terminated polyethylene having: (i) at least 50% allyl chain ends; (ii) a molecular weight distribution of less than or equal to 4.0; (iii) a $g'_{(vts)}$ of 0.95 or less; (iv) a Mn (^1H NMR) of at least 7,000 g/mol; and (v) a Mn (GPC)/Mn (^1H NMR) in the range of from about 0.8 to about 1.2. Preferably, the vinyl terminated ethylene polymers are made according to the process (and using the catalyst systems) described in (U.S. Ser. No. 61/704,604, filed Sep. 24, 2012, entitled, Production of Vinyl Terminated Polyethylene).

In any of the polymerizations described herein, the activator may be an alumoxane, an aluminum alkyl, a stoichiometric activator (also referred to as an ionizing activator), which may be neutral or ionic, and/or a conventional-type cocatalyst, unless otherwise stated. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, stoichiometric activators, and ionizing anion precursor compounds that abstract one reactive, σ -bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

Alumoxane Activators

In an embodiment of the invention, alumoxane activators are utilized as an activator in the catalyst composition, preferably methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane, and/or isobutylalumoxane. Preferably, the activator is a TMA-depleted activator (where TMA means trimethylaluminum). Any method known in the art to remove TMA may be used. For example, to produce a TMA-depleted activator, a solution of alumoxane (such as methylalumoxane), for example, 30 wt % in toluene may be diluted in toluene and the aluminum alkyl (such as TMA in the case of MAO) is removed from the solution, for example, by combination with trimethylphenol and filtration of the solid. In such embodiments, the TMA-depleted activator comprises from about 1 wt % to about 14 wt % trimethylaluminum (preferably less than 13 wt %, preferably less than 12 wt %, preferably less than 10 wt %, preferably less than 5 wt %, or preferably 0 wt %, or, optionally, greater than 0 wt % or greater than 1 wt %).

Stoichiometric Activators

The catalyst systems useful herein may comprise one or more stoichiometric activators. A stoichiometric activator is a non-alumoxane compound which when combined in a reaction with the catalyst compound (such as a metallocene compound) forms a catalytically active species, typically at molar ratios of stoichiometric activator to metallocene compound of 10:1 or less (preferably 5:1, more preferably 2:1, or even more preferably 1:1), however is within the scope of this invention to use a molar ratio of stoichiometric activator to metallocene compound of greater than 10:1 as well. Useful stoichiometric (or non-alumoxane) activator-to-catalyst ratios range from 0.5:1 to 10:1, preferably 1:1 to 5:1, although

ranges of from 0.1:1 to 100:1, alternately from 0.5:1 to 200:1, alternately from 1:1 to 500:1 alternately from 1:1 to 1000:1 may be used.

Stoichiometric activators are non-alumoxane compounds which may be neutral or ionic, such as tri(n-butyl) ammonium tetrakis(pentafluorophenyl)borate, a tris perfluorophenyl boron metalloid precursor, or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Pat. No. 5,942,459), or a combination thereof. It is also within the scope of this invention to use stoichiometric activators alone or in combination with alumoxane or modified alumoxane activators.

Neutral Stoichiometric Activators

Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogens, substituted alkyls, aryls, arylhalides, alkoxy, and halides. Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds, and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms, and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl, or mixtures thereof. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. Most preferably, the neutral stoichiometric activator is tris perfluorophenyl boron or tris perfluoronaphthyl boron.

Ionic Stoichiometric Activators

Ionic stoichiometric activators may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining anion of the activator. Such compounds and the like are described in European Publication Nos. EP 0 570 982 A; EP 0 520 732 A; EP 0 495 375 A; EP 0 500 944 B1; EP 0 277 003 A; EP 0 277 004 A; U.S. Pat. Nos. 5,153,157; 5,198,401; 5,066,741; 5,206,197; 5,241,025; 5,384,299; 5,502,124; and U.S. patent application Ser. No. 08/285,380, filed Aug. 3, 1994; all of which are herein fully incorporated by reference.

Ionic stoichiometric activators comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion. Preferably, the anion is relatively large (bulky), capable of stabilizing the catalytically active species (preferably a group 4 catalytically active species) which is formed when the catalyst (such as a metallocene compound) and the stoichiometric activator are combined. Preferably, the anion will be sufficiently labile to be displaced by olefinic, diolefinic, and acetylenically unsaturated substrates or other neutral Lewis bases, such as ethers, amines, and the like. Two classes of useful compatible non-coordinating anions have been disclosed in EP 0 277,003 A and EP 0 277,004 A: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms, such as carboranes, metallacarboranes, and boranes.

Ionic stoichiometric activators comprise an anion, preferably a non-coordinating anion. The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so

as to cause it to form a neutral four coordinate metallocene compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with this invention are those that are compatible, stabilize the catalyst (such as metallocene) cation in the sense of balancing its ionic charge at +1, yet retain sufficient lability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization.

In a preferred embodiment of this invention, the ionic stoichiometric activators are represented by the following formula (1):



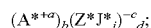
wherein $(Z)_d^+$ is the cation component and A^{d-} is the anion component; where Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; (L-H)⁺ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3.

When Z is (L-H) such that the cation component is (L-H)_d⁺, the cation component may include Bronsted acids such as protonated Lewis bases capable of protonating a moiety, such as an alkyl or aryl, from the bulky ligand metallocene containing transition metal catalyst precursor, resulting in a cationic transition metal species. Preferably, the activating cation (L-H)_d⁺ is a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers, such as dimethyl ether diethyl ether, tetrahydrofuran, and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof.

When Z is a reducible Lewis acid, $(Z)_d^+$ is preferably represented by the formula: $(Ar_3C)^+$, where Ar is aryl or aryl substituted with a heteroatom, a C₁ to C₄₀ hydrocarbyl, or a substituted C₁ to C₄₀ hydrocarbyl, preferably $(Z)_d^+$ is represented by the formula: $(Ph_3C)^+$, where Ph is phenyl or phenyl substituted with a heteroatom, a C₁ to C₄₀ hydrocarbyl, or a substituted C₁ to C₄₀ hydrocarbyl. In a preferred embodiment, the reducible Lewis acid is triphenyl carbenium.

The anion component A^{d-} includes those having the formula $[M^{k+}Q_n]^{d-}$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6, preferably 3, 4, 5, or 6; (n-k)=d; M is an element selected from group 13 of the Periodic Table of the Elements, preferably boron or aluminum; and each Q is, independently, a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than one occurrence is Q a halide, and two Q groups may form a ring structure. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} components also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

In other embodiments of this invention, the ionic stoichiometric activator may be an activator comprising expanded anions, represented by the formula:



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wherein A* is a cation having charge +a; Z* is an anion group of from 1 to 50 atoms not counting hydrogen atoms, further containing two or more Lewis base sites; J* independently each occurrence is a Lewis acid coordinated to at least one Lewis base site of Z*, and optionally two or more such J* groups may be joined together in a moiety having multiple Lewis acid functionality; j is a number from 2 to 12; and a, b, c, and d are integers from 1 to 3, with the proviso that axb is equal to cxd. Examples of such activators comprising expandable anions may be found in U.S. Pat. No. 6,395,671, which is fully incorporated herein by reference.

Examples of ionic stoichiometric activators useful in the catalyst system of this invention are:

trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetraphenylborate, tropillium tetraphenylborate, triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(pentafluorophenyl)borate, tropillium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylphosphonium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate, benzene(diazonium)tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, benzene(diazonium)tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium)tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis

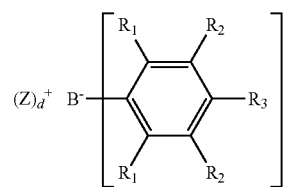
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(perfluorobiphenyl)borate, tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium)tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, benzene(diazonium)tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and dialkyl ammonium salts such as: di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium tetrakis(pentafluorophenyl)borate; and additional trisubstituted phosphonium salts such as tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate, and tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate.

Most preferably, the ionic stoichiometric activator is N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium tetrakis(perfluorophenyl)borate.

Bulky Ionic Stoichiometric Activators

"Bulky activator" as used herein refers to ionic stoichiometric activators represented by the formula:



where:

each R₁ is, independently, a halide, preferably a fluoride;
each R₂ is, independently, a halide, a C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula —O—Si—R_a, where R_a is a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl or hydrocarbylsilyl group (preferably R₂ is a fluoride or a perfluorinated phenyl group);
each R₃ is a halide, C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula —O—Si—R_a, where R_a is a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl or hydrocarbylsilyl group (preferably R₃ is a fluoride or a C₆ perfluorinated aromatic hydrocarbyl group);

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wherein R_2 and R_3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R_2 and R_3 form a perfluorinated phenyl ring); $(Z)_d^+$ is the cation component; where Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; (L-H)⁺ is a Bronsted acid; and d is an integer from 1 to 3; wherein the boron anion component has a molecular weight of greater than 1020 g/mol; and wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å, alternately greater than 300 cubic Å, or alternately greater than 500 cubic Å.

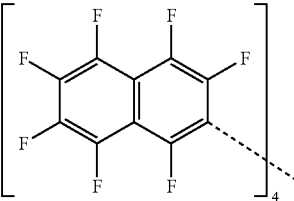
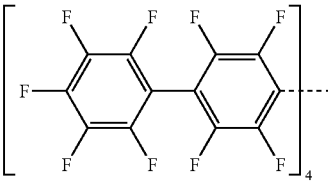
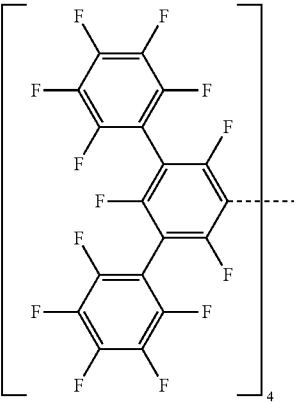
“Molecular volume” is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered “less bulky” in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered “more bulky” than a substituent with a smaller molecular volume.

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mula of the substituent using the following table of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring.

Element	Relative Volume
H	1
1 st short period, Li to F	2
2 nd short period, Na to Cl	4
1 st long period, K to Br	5
2 nd long period, Rb to I	7.5
3 rd long period, Cs to Bi	9

Exemplary bulky substituents of activators suitable herein and their respective scaled volumes and molecular volumes are shown in the table below. The dashed bonds indicate binding to boron, as in the general formula above.

Activator	Structure of boron substituents	Molecular Formula of each substituent	V_s	MV Per subst. (Å ³)	Total MV (Å ³)
Dimethylanilinium tetrakis(perfluoronaphthyl)borate		$C_{10}F_7$	34	261	1044
Dimethylanilinium tetrakis(perfluorobiphenyl)borate		$C_{12}F_9$	42	349	1396
[4-tButyl—PhNMe ₂ H] [(C ₆ F ₃ (C ₆ F ₅) ₂) ₄ B]		$C_{18}F_{13}$	62	515	2060

Molecular volume may be calculated as reported in “A Simple ‘Back of the Envelope’ Method for Estimating the Densities and Molecular Volumes of Liquids and Solids,” Journal of Chemical Education, Vol. 71, No. 11, November 1994, pp. 962-964. Molecular volume (MV), in units of cubic Å, is calculated using the formula: $MV = 8.3V_s$, where V_s is the scaled volume. V_s is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular for-

Exemplary bulky ionic stoichiometric activators useful in catalyst systems herein include: trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis

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(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium)tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium)tetrakis(perfluorobiphenyl)borate, [4-t-butyl-PhNMe₂H][[(C₆F₅)₂]₄B], (where Ph is phenyl and Me is methyl), and the types disclosed in U.S. Pat. No. 7,297,653.

In another embodiment of this invention, an activation method using ionic compounds not containing an active proton but capable of producing a bulky ligand metallocene catalyst cation and their non-coordinating anion are also contemplated, and are described in EP 0 426 637 A, EP 0 573 403 A, and U.S. Pat. No. 5,387,568, which are all herein incorporated by reference.

In another embodiment of this invention, inventive processes also can employ stoichiometric activator compounds that are initially neutral Lewis acids but form a cationic metal complex and a noncoordinating anion, or a zwitterionic complex upon reaction with the metallocene compounds. For example, tris(pentafluorophenyl) boron or aluminum may act to abstract a hydrocarbyl or hydride ligand to yield an invention cationic metal complex and stabilizing noncoordinating anion, see EP 0 427 697 A and EP 0 520 732 A for illustrations of analogous group 4 metallocene compounds. Also, see the methods and compounds of EP 0 495 375 A. For formation of zwitterionic complexes using analogous group 4 compounds, see U.S. Pat. Nos. 5,624,878; 5,486,632; and 5,527,929.

In another embodiment of this invention, another suitable ionic stoichiometric activator comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein X^{e+} is a cationic oxidizing agent having a charge of e+; e is 1, 2, or 3; A^{d-} is a non-coordinating anion having the charge d-; and d is 1, 2, or 3. Examples of X^{e+} include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag⁺, or Pb²⁺. Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted acid containing activators, especially tetrakis(pentafluorophenyl)borate.

Activator Combinations

It is within the scope of this invention that metallocene compounds can be combined with one or more activators or activation methods described above. For example, a combination of activators have been described in U.S. Pat. Nos. 5,153,157; 5,453,410; European Publication No. EP 0 573 120 B1; PCT Publication Nos. WO 94/07928; and WO 95/14044. These documents all discuss the use of an alumoxane in combination with a stoichiometric activator.

In another embodiment, the vinyl terminated macromonomer may be a vinyl terminated ethylene macromonomer. In some embodiments, a phenoxyimine-based catalyst (a Mitsui

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FI catalyst) or a pyrroleimine-based catalyst (a Mitsui PI catalyst) can be used to prepare the vinyl terminated ethylene macromonomer. These catalysts comprise (a) a transition metal (preferably Ti) compound having phenoxyimine or pyrroleimine as a ligand, and (b) one or more kind(s) of compound selected from (b-1) an organic metal compound, (b-2) an organic aluminumoxy compound, and (b-3) a compound that reacts with the transition metal compound (a) to form an ion pair, as described in Japanese Publication Nos. JP-A-2001-72706, JP-A-2002-332312, JP-A-2003-313247, JP-A-2004-107486, and JP-A-2004-107563. Herein, as the transition metal contained in the transition metal compound, the transition metal of Groups 3 to 11 in the periodic table can be used. Preferred catalysts to prepare the vinyl terminated ethylene macromonomer include those described in U.S. Pat. No. 7,795,347, specifically at column 16, line 56 et seq. in Formula (XI).

In another embodiment, the vinyl terminated macromonomer may be a vinyl terminated isotactic polypropylene or a vinyl terminated polyethylene as disclosed in U.S. Pat. Nos. 6,444,773; 6,555,635; 6,147,180; 6,660,809; 6,750,307; 6,774,191; 6,169,154; and European Publication No. EP 0 958 309, which are incorporated by reference herein.

In a preferred embodiment, any vinyl terminated macromonomer described herein can be fractionated or distilled by any means known in the art and one or more of the fractions may be used in the invention described herein. Preferred fractions typically have a narrow Mw/Mn, such as less than 1.5, preferably 1.4 or less, preferably 1.3 or less, preferably 1.2 or less. Alternately, the Mw/Mn is from 1 to 1.4, preferably 1.05 to 1.3, preferably 1.1 to 1.2.

In another embodiment of the invention, the fractions have a narrow boiling point range (as determined by ASTM D86) of less than 70° C., preferably less than 60° C., preferably less than 50° C., preferably less than 40° C., preferably less than 30° C., preferably less than 20° C., preferably less than 10° C.

In a preferred embodiment of the invention, the vinyl terminated macromonomer injected into a gas chromatograph column to determine the optimum cut points for the fractionation.

In a preferred embodiment, the fractions may be obtained by separation of the vinyl terminated macromonomer product such as by the processes described in GB 1550419A; U.S. Pat. Nos. 3,647,906; and 3,592,866. Useful fractions include ranges from about 4 carbon-numbers up to 20 carbon-numbers, e.g., C₄-C₈, C₄-C₁₄, C₄-C₂₀. The lower α-olefin fraction may contain α-olefins having the same carbon-number as the lowest α-olefin in the higher α-olefin fraction, but preferably contains only α-olefins of carbon-numbers lower than the carbon-number of the lowest α-olefin in the higher α-olefin fraction. The higher α-olefin fraction may include α-olefins of the same carbon number as the highest α-olefin in the lower α-olefin fraction up to the highest α-olefin produced in the reaction, but generally not higher than C₄₀. Preferably, however, the higher α-olefin fraction contains only α-olefins of carbon-numbers higher than the carbon number of the highest α-olefin in the lower α-olefin fraction.

In a separation where an α-olefin product mixture free of light oligomers, e.g., dimers, trimers, tetramers, etc., is desired, the lower α-olefin fraction is further separated into a light α-olefin fraction and an intermediate α-olefin fraction. The light α-olefin fraction may include from C₄ up to C₁₂, e.g., C₄-C₆, C₄-C₈, C₄-C₁₀, etc. In this modification, the intermediate α-olefin fraction is removed as product and the light α-olefin fraction is converted to additional intermediate α-olefins.

In another embodiment, any vinyl terminated macromonomer described herein can be separated into different boiling point cuts by distillation performed according to the procedures described in ASTM methods D2892 and D5236. (D2892: Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column) and D5236: Standard Test Method for Distillation of Heavy Hydrocarbon Mixtures (Vacuum Potstill Method).)

For example, a low molecular weight atactic polypropylene VTM (677.3 gram charge) can be fractionated or distilled using the boiling point range, mass recovery, vacuum conditions listed below. Both initial boiling point (IBP) and final boiling point (FBP) are in degree Fahrenheit (° F.) and corrected to atmospheric pressure.

Fraction (Cut) #	Initial boiling point/IBP (° F.)	Final boiling point/FBP (° F.)	Weight of collected fraction (grams)	Still pressure (mmHg)	ASTM method used
Charge (Feed)	—	—	677.3		
1	IBP	140	3.8	760	D2892
2	140	160	11.9	760	D2892
3	160	265	27.8	760	D2892
4	265	365	35.0	88	D2892
5	365	465	46.6	88	D2892
6	465	525	34.4	88	D2892
7	525	568	44.0	10	D2892
8	568	588	14.2	10	D2892
9	588	645	53.1	10	D2892
10	645	700	63.4	2	D2892
11	700	844	41.2	0.2	D5236
12	844	892	42.3	0.2	D5236
13	892	904	17.9	0.2	D5236
Distillation Bottoms	904+	—	226.6	—	—

As shown in the table above, total recovery of collected fractions (fraction 1 to 13) with boiling points between room temperature and 904° F. was 435.6 g (64.3 wt % of initial charge). Total recovery of distillation bottoms with boiling point above 904° F. was 226.6 g (33.5 wt % of initial charge). The total recovery of both distilled fractions and bottoms material amounts to 97.8 wt %. The resulting distilled fractions and distillation bottoms have narrow molecular weight distributions (Mw/Mn<1.4) as determined by GPC.

In another embodiment of the invention, the vinyl terminated macromonomer (preferably a propylene based vinyl terminated macromonomer, preferably a homopolypropylene vinyl terminated macromonomer) has less than 1 mol % regio defects (as determined by ¹³C NMR), based upon the total propylene monomer. Three types of defects are defined to be the regio defects: 2,1-erythro, 2,1-threo, and 3,1-isomerization. The structures and peak assignments for these are given in L. Resconi, L. Cavallo, A. Fait, and F. Piemontesi, Chem. Rev. 2000, 100, pp. 1253-1345, as well as H. N. Cheng, Macromolecules, 17, p. 1950 (1984). Alternately, the vinyl terminated macromonomer (preferably a propylene based vinyl terminated macromonomer, preferably a homopolypropylene vinyl terminated macromonomer) has less than 250 regio defects per 10,000 monomer units (as determined by ¹³C NMR), preferably less than 150, preferably less than 100, preferably less than 50 regio defects per 10,000 monomer units. The regio defects each give rise to multiple peaks in the carbon NMR spectrum, and these are all integrated and averaged (to the extent that they are resolved from other peaks in the spectrum), to improve the measurement accuracy. The chemical shift offsets of the resolvable resonances used in the analysis are tabulated below. The precise peak positions may shift as a function of NMR solvent choice.

Regio defect	Chemical shift range (ppm)
2,1-erythro	42.3, 38.6, 36.0, 35.9, 31.5, 30.6, 17.6, 17.2
2,1-threo	43.4, 38.9, 35.6, 34.7, 32.5, 31.2, 15.4, 15.0
3,1 insertion	37.6, 30.9, 27.7

The average integral for each defect is divided by the integral for one of the main propylene signals (CH₃, CH, CH₂), and multiplied by 10,000 to determine the defect concentration per 10,000 monomers.

In another embodiment, any vinyl terminated macromonomer described herein may have a melting point (DSC first melt) of from 60° C. to 160° C., alternately 50° C. to 145° C.,

alternately 50° C. to 130° C., alternately 50° C. to 100° C. In another embodiment, the vinyl terminated macromonomer described herein have no detectable melting point by DSC following storage at ambient temperature (23° C.) for at least 48 hours.

In another embodiment, any vinyl terminated macromonomer described herein may have a glass transition temperature of less than 0° C. or less (DSC), preferably -10° C. or less, more preferably -20° C. or less, more preferably -30° C. or less, more preferably -50° C. or less.

Melting temperature (*T_m*) and glass transition temperature (*T_g*) are measured using Differential Scanning Calorimetry (DSC) using commercially available equipment such as a TA Instruments 2920 DSC. Typically, 3 to 10 mg of the sample, that has been stored at room temperature for at least 48 hours, is sealed in an aluminum pan and loaded into the instrument at room temperature. The sample is equilibrated at 25° C., then it is cooled at a cooling rate of 10° C./min to -80° C. The sample is held at -80° C. for 5 min and then heated at a heating rate of 10° C./min to 25° C. The glass transition temperature is measured from the heating cycle. Alternatively, the sample is equilibrated at 25° C., then heated at a heating rate of 10° C./min to 150° C. The endothermic melting transition, if present, is analyzed for onset of transition and peak temperature. The melting temperatures reported are the peak melting temperatures from the first heat unless otherwise specified. For samples displaying multiple peaks, the melting point (or melting temperature) is defined to be the peak melting temperature (i.e., associated with the largest endothermic calorimetric response in that range of temperatures) from the DSC melting trace.

In another embodiment, the vinyl terminated macromonomers described herein are a liquid at 25° C.

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In a particularly preferred embodiment of the invention, the vinyl terminated macromonomer (preferably comprising propylene, at least 50 mol % propylene, preferably at least 70 propylene) has less than 250 regio defects per 10,000 monomer units, preferably less than 150, preferably less than 100, preferably less than 50 regio defects per 10,000 monomer units and a Tg of less than 0° C. or less (DSC), preferably -10° C. or less, more preferably -20° C. or less, more preferably -30° C. or less, more preferably -50° C. or less.

In another embodiment, the vinyl terminated macromonomers useful herein have a viscosity at 60° C. of greater than 1,000 cP, greater than 12,000 cP, or greater than 100,000 cP. In other embodiments, the vinyl terminated macromonomer have a viscosity of less than 200,000 cP, less than 150,000 cP, or less than 100,000 cP. Viscosity is defined as resistance to flow and the melt viscosity of neat copolymers is measured at elevated temperature using a Brookfield Digital Viscometer.

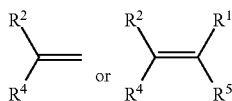
In another embodiment, any VTM described herein has a viscosity (also referred to a Brookfield Viscosity or Melt Viscosity) of 90,000 mPa·sec or less at 190° C. (as measured by ASTM D 3236 at 190° C.; ASTM=American Society for Testing and Materials); or 80,000 mPa·sec or less, or 70,000 mPa·sec or less, or 60,000 mPa·sec or less, or 50,000 mPa·sec or less, or 40,000 mPa·sec or less, or 30,000 mPa·sec or less, or 20,000 mPa·sec or less, or 10,000 mPa·sec or less, or 8,000 mPa·sec or less, or 5,000 mPa·sec or less, or 4,000 mPa·sec or less, or 3,000 mPa·sec or less, or 1,500 mPa·sec or less, or between 250 and 6000 mPa·sec, or between 500 and 5,500 mPa·sec, or between 500 and 3,000 mPa·sec, or between 500 and 1,500 mPa·sec, and/or a viscosity of 8,000 mPa·sec or less at 160° C. (as measured by ASTM D 3236 at 160° C.); or 7,000 mPa·sec or less, or 6,000 mPa·sec or less, or 5,000 mPa·sec or less, or 4,000 mPa·sec or less, or 3,000 mPa·sec or less, or 1,500 mPa·sec or less, or between 250 and 6,000 mPa·sec, or between 500 and 5,500 mPa·sec, or between 500 and 3,000 mPa·sec, or between 500 and 1,500 mPa·sec. In other embodiments, the viscosity is 200,000 mPa·sec or less at 190° C., depending on the application. In other embodiments, the viscosity is 50,000 mPa·sec or less depending on the applications.

Titanium Catalysts

Suitable titanium catalysts useful for Diels Alder applications noted herein include, for example, dichlorobis(isopropoxy)titanium, titanium tetrachloride, titanium tetrachloride dimethoxyethane complex, triethyl aluminum, tris(pentafluorophenyl)borane, trifluoromethanesulfonimide, trifluoromethanesulfonic acid, methanesulfonic acid, p-toluenesulfonic acid, tin tetrachloride, imidazolidinones, oxazaborolidinones, and alumina- or silica-supported aluminum or titanium reagents.

Vinyl and Vinylene Monomers

Vinyl and vinylene monomers useful herein include those represented by the formulae:



wherein R¹, R², R⁴ and R⁵ are each, independently, a hydrogen atom or a C₁ to a C₄₀ hydrocarbyl moiety.

Useful monomers include, for example, ethylene, propylene and/or C₄ to C₄₀ olefins, preferably ethylene and/or C₅ to C₂₅ olefins, or preferably ethylene and/or C₆ to C₁₈ olefins. The C₄ to C₄₀ olefin monomers may be linear, branched,

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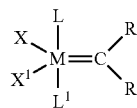
or cyclic. The C₄ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups. Exemplary, C₄ to C₄₀ olefin monomers include butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives.

In another embodiment, the monomer can be a vinyl terminated macromonomer (VTM) as described herein.

Alkene Metathesis Catalysts

An alkene metathesis catalyst is a compound that catalyzes the reaction between a first olefin (typically vinyl) with a second olefin (typically vinyl or vinylene) to produce a product, typically with the elimination of ethylene.

In a preferred embodiment, the alkene metathesis catalyst useful herein is represented by the Formula (I):



Formula (I)

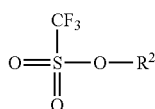
where:

M is a Group 8 metal, preferably Ru or Os, preferably Ru;
X and X¹ are, independently, any anionic ligand, preferably a halogen (preferably chlorine), an alkoxide or a triflate, or X and X¹ may be joined to form a dianionic group and may form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms;
L and L¹ are, independently, a neutral two electron donor, preferably a phosphine or a N-heterocyclic carbene, L and L¹ may be joined to form a single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms;
L and X may be joined to form a multidentate monoanionic group and may form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms;
L¹ and X¹ may be joined to form a multidentate monoanionic group and may form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms;
R and R¹ are, independently, hydrogen or C₁ to C₃₀ substituted or unsubstituted hydrocarbyl (preferably a C₁ to C₃₀ substituted or unsubstituted alkyl or a substituted or unsubstituted C₄ to C₃₀ aryl);
R¹ and L¹ or X¹ may be joined to form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms; and
R and L or X may be joined to form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms.

Preferred alkoxides include those where the alkyl group is a phenol, substituted phenol (where the phenol may be substituted with up to 1, 2, 3, 4, or 5 C₁ to C₁₂ hydrocarbyl groups) or a C₁ to C₁₀ hydrocarbyl, preferably a C₁ to C₁₀ alkyl group, preferably methyl, ethyl, propyl, butyl, or phenyl.

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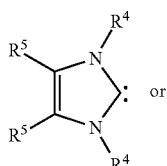
Preferred triflates are represented by the Formula (II):



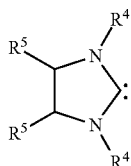
Formula (II)

where R² is hydrogen or a C₁ to C₃₀ hydrocarbyl group, preferably a C₁ to C₁₂ alkyl group, preferably methyl, ethyl, propyl, butyl, or phenyl.

Preferred N-heterocyclic carbenes are represented by the Formula (III) or the Formula (IV):



Formula (III)



Formula (IV)

where:

each R⁴ is independently a hydrocarbyl group or substituted hydrocarbyl group having 1 to 40 carbon atoms, preferably methyl, ethyl, propyl, butyl (including isobutyl and n-butyl), pentyl, cyclopentyl, hexyl, cyclohexyl, octyl, cyclooctyl, nonyl, decyl, cyclodecyl, dodecyl, cyclododecyl, mesityl, adamantyl, phenyl, benzyl, tolyl, chlorophenyl, phenol, substituted phenol, or CH₂C(CH₃)₃; and each R⁵ is hydrogen, a halogen, or a C₁ to C₁₂ hydrocarbyl group, preferably hydrogen, bromine, chlorine, methyl, ethyl, propyl, butyl, or phenyl.

In other useful embodiments, one of the N groups bound to the carbene in formula (III) or (IV) is replaced with an S, O, or P atom, preferably an S atom.

Other useful N-heterocyclic carbenes include the compounds described in Hermann, W. A. Chem. Eur. J., 1996, 2, pp. 772 and 1627; Enders, D. et al. Angew. Chem. Int. Ed., 1995, 34, p. 1021; Alder R. W., Angew. Chem. Int. Ed., 1996, 35, p. 1121; and Bertrand, G. et al., Chem. Rev., 2000, 100, p. 39.

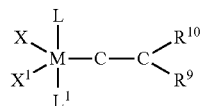
In a preferred embodiment, the alkene metathesis catalyst is one or more of tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene][3-phenyl-1H-inden-1-ylidene]ruthenium(II) dichloride, tricyclohexylphosphine[3-phenyl-1H-inden-1-ylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(II) dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(II) dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylenetruthenium(II) dichloride, and [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-[2-[(4-

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methylphenyl)imino]methyl]-4-nitrophenolyl]-[3-phenyl-1H-inden-1-ylidene]ruthenium(II) chloride. In a preferred embodiment, the catalyst is 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylenetruthenium(II) dichloride and/or Tricyclohexylphosphine[3-phenyl-1H-inden-1-ylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(II) dichloride.

In another embodiment, the alkene metathesis catalyst is represented by Formula (I) above, where: M is Os or Ru; R¹ is hydrogen; X and X¹ may be different or the same and are any anionic ligand; L and L¹ may be different or the same and are any neutral electron donor; and R may be hydrogen, substituted or unsubstituted alkyl, or substituted or unsubstituted aryl. R is preferably hydrogen, C₁ to C₂₀ alkyl, or aryl. The C₁ to C₂₀ alkyl may optionally be substituted with one or more aryl, halide, hydroxy, C₁ to C₂₀ alkoxy, or C₂ to C₂₀ alkoxy carbonyl groups. The aryl may optionally be substituted with one or more C₁ to C₂₀ alkyl, aryl, hydroxyl, C₁ to C₅ alkoxy, amino, nitro, or halide groups. L and L¹ are preferably phosphines of the formula PR³ⁱR⁴ⁱR⁵ⁱ, where R³ⁱ is a secondary alkyl or cycloalkyl, and R⁴ⁱ and R⁵ⁱ are aryl, C₁ to C₁₀ primary alkyl, secondary alkyl, or cycloalkyl. R⁴ⁱ and R⁵ⁱ may be the same or different. L and L¹ are preferably the same and are —P(cyclohexyl)₃, —P(cyclopentyl)₃, or —P(isopropyl)₃. X and X¹ are most preferably the same and are chlorine.

In another embodiment of the present invention, the ruthenium and osmium carbene compounds have the Formula (V):



Formula (V)

where M is Os or Ru, preferably Ru; X, X¹, L, and L¹ are as described above; and R⁹ and R¹⁰ may be different or the same and may be hydrogen, substituted or unsubstituted alkyl, or substituted or unsubstituted aryl. The R⁹ and R¹⁰ groups may optionally include one or more of the following functional groups: alcohol, thiol, ketone, aldehyde, ester, ether, amine, imine, amide, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, and halogen groups. Such compounds and their synthesis are described in U.S. Pat. No. 6,111,121.

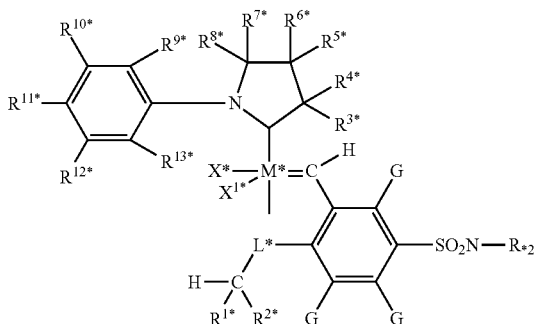
In another embodiment, the alkene metathesis catalyst useful herein may be any of the catalysts described in U.S. Pat. Nos. 6,111,121; 5,312,940; 5,342,909; 7,329,758; 5,831,108; 5,969,170; 6,759,537; 6,921,735; and U.S. Patent Publication No. 2005-0261451 A1, including, but not limited to, benzylidene-bis(tricyclohexylphosphine)dichlororuthenium, benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium, dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(II), (1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium, 1,3-Bis(2-methylphenyl)-2-imidazolidinylidene]dichloro(2-isopropoxyphenylmethylene) ruthenium(II), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro[3-(2-pyridinyl)propylidene]ruthenium(II), [1,3-Bis(2-methylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene) (tricyclohexylphosphine)ruthenium(II), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(3-methyl-2-butenylidene) (tricyclohexylphos-

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phine)ruthenium(II), and [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(benzylidene)bis(3-bromopyridine)ruthenium(II).

In another embodiment, the alkene metathesis catalyst is represented by the formula:

Formula (VI)



where:

M* is a Group 8 metal, preferably Ru or Os, preferably Ru; X* and X1* are, independently, any anionic ligand, preferably a halogen (preferably C₁), an alkoxide or an alkyl sulfonate, or X and X1 may be joined to form a dianionic group and may form single ring of up to 30 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms;

L* is N, O, P, or S, preferably N or O;

R* is hydrogen or a C₁ to C₃₀ hydrocarbyl or substituted hydrocarbyl, preferably methyl;

R^{1*}, R^{2*}, R^{3*}, R^{4*}, R^{5*}, R^{6*}, R^{7*}, and R^{8*} are, independently, hydrogen or a C₁ to C₃₀ hydrocarbyl or substituted hydrocarbyl, preferably methyl, ethyl, propyl or butyl, preferably R^{1*}, R^{2*}, R^{3*}, and R^{4*} are methyl;

each R^{9*} and R^{13*} are, independently, hydrogen or a C₁ to C₃₀ hydrocarbyl or substituted hydrocarbyl, preferably a C₂ to C₆ hydrocarbyl, preferably ethyl;

R^{10*}, R^{11*}, R^{12*} are, independently hydrogen or a C₁ to C₃₀ hydrocarbyl or substituted hydrocarbyl, preferably hydrogen or methyl;

each G, is, independently, hydrogen, halogen or C₁ to C₃₀ substituted or unsubstituted hydrocarbyl (preferably a C₁ to C₃₀ substituted or unsubstituted alkyl or a substituted or unsubstituted C₄ to C₃₀ aryl);

where any two adjacent R groups may form a single ring of up to 8 non-hydrogen atoms or a multinuclear ring system of up to 30 non-hydrogen atoms.

Preferably, any two adjacent R groups may form a fused ring having from 5 to 8 non hydrogen atoms. Preferably the non-hydrogen atoms are C and/or O. Preferably the adjacent R groups form fused rings of 5 to 6 ring atoms, preferably 5 to 6 carbon atoms. By adjacent is meant any two R groups located next to each other, for example R^{3*} and R^{4*} can form a ring and/or R^{11*} and R^{12*} can form a ring.

In a preferred embodiment, the metathesis catalyst compound comprises one or more of: 2-(2,6-diethylphenyl)-3,5,5,5-tetramethylpyrrolidine[2-(i-propoxy)-5-(N,N-dimethylamino sulfonyl)phenyl]methylene ruthenium dichloride; 2-(mesityl)-3,3,5,5-tetramethylpyrrolidine[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium dichloride; 2-(2-isopropyl)-3,3,5,5-tetramethylpyrrolidine [2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium dichloride; 2-(2,6-diethyl-4-fluorophe-

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nyl)-3,3,5,5-tetramethylpyrrolidine[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium dichloride, or mixtures thereof.

For further information on such alkene metathesis catalysts, please see U.S. Ser. No. 12/939,054, filed Nov. 3, 2010, claiming priority to and the benefit of U.S. Ser. No. 61/259,514, filed Nov. 9, 2009.

The above named catalysts are generally available for Sigma-Aldrich Corp. (St. Louis, Mo.) or Strem Chemicals, Inc. (Newburyport, Mass.).

In a preferred embodiment of the present invention, the invention relates to a metathesis catalyst comprising: a Group 8 metal complex represented by the formula (H):



wherein

M'' is a Group 8 metal (preferably M is ruthenium or osmium, preferably ruthenium);

each X'' is independently an anionic ligand (preferably selected from the group consisting of halides, alkoxides, aryloxides, and alkyl sulfonates, preferably a halide, preferably chloride);

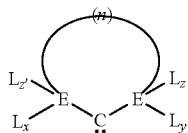
Rⁿ¹ and Rⁿ² are independently selected from the group consisting of hydrogen, a C₁ to C₃₀ hydrocarbyl, and a C₁ to C₃₀ substituted hydrocarbyl (preferably Rⁿ¹ and Rⁿ² are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl, octyl, cyclooctyl, and substituted analogs and isomers thereof, preferably selected from the group consisting of tert-butyl, sec-butyl, cyclohexyl, and cyclooctyl);

Rⁿ³ and Rⁿ⁴ are independently selected from the group consisting of hydrogen, C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides (preferably Rⁿ³ and Rⁿ⁴ are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl, octyl, cyclooctyl, and substituted analogs and isomers thereof, preferably selected from the group consisting of tert-butyl, sec-butyl, cyclohexyl, and cyclooctyl); and

L'' is a neutral donor ligand, preferably L'' is selected from the group consisting of a phosphine, a sulfonated phosphine, a phosphite, a phosphinite, a phosphonite, an arsine, a stibine, an ether, an amine, an imine, a sulfoxide, a carboxyl, a nitrosyl, a pyridine, a thioester, a cyclic carbene, and substituted analogs thereof; preferably a phosphine, a sulfonated phosphine, an N-heterocyclic carbene, a cyclic alkyl amino carbene, and substituted analogs thereof (preferably L'' is selected from a phosphine, an N-heterocyclic carbene, a cyclic alkyl amino carbene, and substituted analogs thereof).

A "cyclic carbene" may be defined as a cyclic compound with a neutral dicoordinate carbon center featuring a lone pair of electrons. Such cyclic carbenes may be represented by the formula (IV) below:

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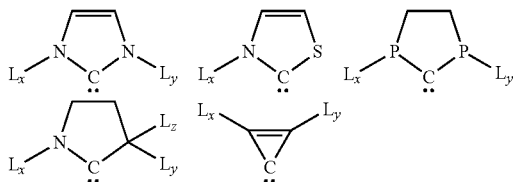
where

n is a linking group comprising from one to four ring vertices selected from the group consisting of C, Si, N, P, O, and S, with available valences optionally occupied by H, oxo, hydrocarbyl, or substituted hydrocarbyl groups; preferably, n comprises two ring vertices of carbon with available valences occupied by H, oxo, hydrocarbyl or substituted hydrocarbyl groups; preferably n is C₂H₂, C₂H₄, or substituted versions thereof;

each E is independently selected from the group comprising C, N, S, O, and P, with available valences optionally occupied by Lx, Ly, Lz, and Lz'; preferably, at least one E is a C; preferably, one E is a C and the other E is a N; preferably, both E's are C; and

Lx, Ly, Lz, and Lz' are independently selected from the group comprising hydrogen, hydrocarbyl groups, and substituted hydrocarbyl groups; preferably, Lx, Ly, Lz, and Lz' are independently selected from the group comprising a hydrocarbyl group and substituted hydrocarbyl group having 1 to 40 carbon atoms; preferably, Lx, Ly, Lz, and Lz' are independently selected from the group comprising C₁₋₁₀ alkyl, substituted C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, substituted C₂₋₁₀ alkenyl, C₂₋₁₀ alkynyl, substituted C₂₋₁₀ alkynyl, aryl, and substituted aryl; preferably, Lx, Ly, Lz, and Lz' are independently selected from the group comprising methyl, ethyl, propyl, butyl (including isobutyl and n-butyl), pentyl, cyclopentyl, hexyl, cyclohexyl, octyl, cyclooctyl, nonyl, decyl, cyclodecyl, dodecyl, cyclododecyl, mesityl, adamantyl, phenyl, benzyl, tolyl, chlorophenyl, 2,6-diethylphenyl, 2,6-diisopropylphenyl, 2-isopropylphenyl, 2-ethyl-6-methylphenyl, 3,5-ditertbutylphenyl, 2-tertbutylphenyl, and 2,3,4,5,6-pentamethylphenyl. Useful substituents include C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, C₂₋₁₀ alkynyl, aryl, C₁₋₁₀ alkoxy, C₂₋₁₀ alkenyloxy, C₂₋₁₀ alkynyloxy, aryloxy, C₂₋₁₀ alkoxycarbonyl, C₁₋₁₀ alkylthio, C₁₋₁₀ alkylsulfonyl, fluoro, chloro, bromo, iodo, oxo, amino, imine, nitrogen heterocycle, hydroxy, thiol, thiono, phosphorous, and carbene groups.

Examples of cyclic carbenes useful in embodiments of the present invention include:

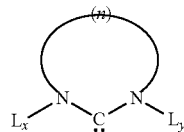


where Lx, Ly, and Lz are as defined above. In some embodiments, at least two of Lx, Ly, Lz, and Lz' may be joined to form a 3- to 12-membered spirocyclic ring, with available valences optionally occupied by H, oxo, halogens, hydrocarbyl or substituted hydrocarbyl groups. Useful substituents include C₁₋₁₀ alkyl, C₂₋₁₀ alkenyl, C₂₋₁₀ alkynyl, aryl, C₁₋₁₀ alkoxy, C₂₋₁₀ alkenyloxy, C₂₋₁₀ alkynyloxy, aryloxy, C₂₋₁₀ alkoxycarbonyl, C₁₋₁₀ alkylthio, C₁₋₁₀ alkylsulfonyl, fluoro,

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chloro, bromo, iodo, oxo, amino, imine, nitrogen heterocycle, hydroxy, thiol, thiono, phosphorous, and carbene groups.

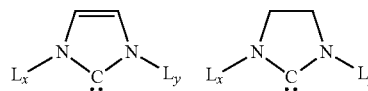
Preferred cyclic carbenes include N-heterocyclic carbenes (NHCs). For purposes of this invention and claims thereto, NHCs are cyclic carbenes of the types described in Formula II above, where each E is N and the available valences on the N are occupied by Lx and Ly. Preferred NHCs may be represented by the formula:



where

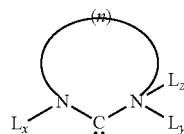
n, Lx, and Ly are as described above in Formula (IV).

Some particularly useful NHCs include:



where Lx and Ly are as described above. Other useful NHCs include the compounds described in Hermann, W. A. Chem. Eur. J. 1996, 2, pp. 772 and 1627; Enders, D. et al., Angew. Chem. Int. Ed. 1995, 34, p. 1021; Alder R. W., Angew. Chem. Int. Ed. 1996, 35, p. 1121; U.S. Ser. No. 61/314,388; and Bertrand, G. et al., Chem. Rev. 2000, 100, p. 39.

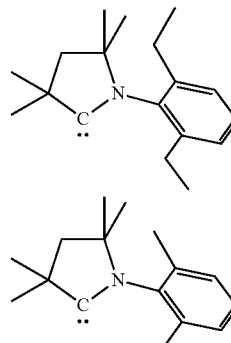
Particularly preferred cyclic carbenes include cyclic alkyl amino carbines (CAACs). In all embodiments herein, CAACs are cyclic carbenes of the types described in Formula II above, where one E is N and the other E is C, and the available valences on the N and C are occupied by Lx, Ly, and Lz. CAACs may be represented by the formula:



where

n, Lx, Ly, and Lz are as described above in Formula (IV).

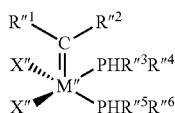
Some particularly useful CAACs include:



Other useful CAACs include the compounds described in U.S. Pat. No. 7,312,331; U.S. Ser. No. 61/259,514; and Bertrand et al, *Angew. Chem. Int. Ed.* 2005, 44, pp. 7236-7239.

Other carbenes useful in embodiments of the present invention include thiazolidenes, P-heterocyclic carbenes (PHCs), and cyclopropenyldenes.

With respect to Group 8 metal complexes of Formula (H), the phosphine ligands (PHRⁿ³Rⁿ⁴) and Lⁿ are neutral donor ligands. In some embodiments, Lⁿ may also be a phosphine having a formula PHRⁿ⁵Rⁿ⁶. In such embodiments, the Group 8 metal complex may be represented by the formula (I):



wherein

Mⁿ is a Group 8 metal (preferably M is ruthenium or osmium, preferably ruthenium);

each Xⁿ is independently an anionic ligand (preferably selected from the group consisting of halides, alkoxides, aryloxides, and alkyl sulfonates, preferably a halide, preferably chloride);

Rⁿ¹ and Rⁿ² are independently selected from the group consisting of hydrogen, a C₁ to C₃₀ hydrocarbyl, and a C₁ to C₃₀ substituted hydrocarbyl (preferably Rⁿ¹ and Rⁿ² are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl, octyl, cyclooctyl, and substituted analogs and isomers thereof, preferably selected from the group consisting of tert-butyl, sec-butyl, cyclohexyl, and cyclooctyl); and

Rⁿ³, Rⁿ⁴, Rⁿ⁵, and Rⁿ⁶ are independently selected from the group consisting of hydrogen, C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides (preferably Rⁿ³, Rⁿ⁴, Rⁿ⁵, and Rⁿ⁶ are independently selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, sec-butyl, pentyl, cyclopentyl, hexyl, cyclohexyl, heptyl, octyl, cyclooctyl, and substituted analogs and isomers thereof, preferably selected from the group consisting of tert-butyl, sec-butyl, cyclohexyl, and cyclooctyl).

With respect to embodiments where Lⁿ is a phosphine having a formula PHRⁿ⁵Rⁿ⁶, in particular embodiments, at least one phosphine ligand is a secondary phosphine ligand. In such embodiments, where at least one of the neutral donor ligands is a secondary phosphine ligand, Rⁿ³ and Rⁿ⁴ or Rⁿ⁵ and Rⁿ⁶ are selected from the group consisting of C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides. In particular embodiments, both donor ligands are secondary phosphine ligands and Rⁿ³, Rⁿ⁴, Rⁿ⁵, and Rⁿ⁶ are selected from the group consisting of C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides.

With respect to embodiments where Lⁿ is a phosphine having a formula PHRⁿ⁵Rⁿ⁶, in particular embodiments, at least one donor ligand is a primary phosphine ligand. In such embodiments where at least one of the phosphine ligands is a primary phosphine ligand, one of Rⁿ³ and Rⁿ⁴ or one of Rⁿ⁵ and Rⁿ⁶ is selected from the group consisting of C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides. In particular embodiments, both donor

ligands are primary phosphine ligands and one of Rⁿ³ and Rⁿ⁴ and one of Rⁿ⁵ and Rⁿ⁶ is selected from the group consisting of C₁ to C₁₂ hydrocarbyl groups, substituted C₁ to C₁₂ hydrocarbyl groups, and halides.

In some embodiments, Rⁿ³ and Rⁿ⁴ form a ring. With respect to embodiments where Lⁿ is a phosphine having a formula PHRⁿ⁵Rⁿ⁶, in particular embodiments, Rⁿ⁵ and Rⁿ⁶ form a ring. In yet other embodiments, Rⁿ³ and Rⁿ⁴ form a ring and Rⁿ⁵ and Rⁿ⁶ form a ring. In other embodiments, Rⁿ³ and at least one of Rⁿ⁵ and Rⁿ⁶ may form a ring, thereby forming a chelating phosphine ligand. In other embodiments, Rⁿ⁴ and at least one of Rⁿ⁵ and Rⁿ⁶ may form a ring, thereby forming a chelating phosphine ligand.

In particular embodiments, the Group 8 metal complex is selected from:

- (I)
- [(HP(tert-butyl)₂)₂Ru(C₅H₈)Cl₂],
 - [(H₂P(tert-butyl))₂Ru(C₅H₈)Cl₂],
 - [(HP(cyclohexyl)₂)₂Ru(C₅H₈)Cl₂],
 - [(H₂P(cyclohexyl))₂Ru(C₅H₈)Cl₂],
 - [(HP(cyclopentyl)₂)₂Ru(C₅H₈)Cl₂],
 - [(H₂P(cyclopentyl))₂Ru(C₅H₈)Cl₂],
 - [(HP(n-butyl)₂)₂Ru(C₅H₈)Cl₂],
 - [(H₂P(n-butyl))₂Ru(C₅H₈)Cl₂],
 - [(HP(sec-butyl)₂)₂Ru(C₅H₈)Cl₂],
 - [(H₂P(sec-butyl))₂Ru(C₅H₈)Cl₂], and
- fluoride and bromide derivatives thereof (preferably, wherein the Cl₂ in the above list is replaced with F₂, Br₂, ClF, ClBr, or FBr).

In embodiments herein, the catalyst systems used may comprise an inert support material.

Hydrogenation

Metathesis products prepared herein can further be hydrogenated after completion or during reaction conditions.

The hydrogenation may be achieved in the presence of any of the known catalysts commonly used for hydrogenating petroleum resins. The catalysts which may be used in the hydrogenation step include the Group 10 metals such as nickel, palladium, ruthenium, rhodium, cobalt and platinum, the Group 6 metals such as tungsten, chromium and molybdenum, and the Group 11 metals such as rhenium, manganese and copper. These metals may be used singularly or in a combination of two or more metals, in the metallic form or in an activated form, and may be used directly or carried on a solid support such as alumina or silica-alumina. A preferred catalyst is one comprising sulfided nickel-tungsten on a gamma-alumina support having a fresh catalyst surface area ranging from 120 to 300 m²/g and containing from 2% to 10% by weight nickel and from 10% to 25% by weight tungsten as described in U.S. Pat. No. 4,629,766. The hydrogenation is carried out with a hydrogen pressure of 20-300 atmospheres, preferably 150-250 atmospheres.

Hot Melt Adhesives

In a particular embodiment, the compositions of this invention can be used in a hot melt adhesive composition. Hot melt adhesives exist as a solid at ambient temperature and can be converted into a tacky liquid by the application of heat. Hot melt adhesives are typically applied to a substrate in molten form.

The adhesive composition includes the inventive polymer described herein. The polymer may be functionalized with maleic acid or maleic anhydride. Additional components may be combined with the polymers or formulations of the polymers to form the adhesive composition.

In one aspect, the adhesive composition can include one or more tackifiers. The tackifiers can include aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadi-

ene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, hydrogenated rosin acids, hydrogenated rosin acids, hydrogenated rosin esters, derivatives thereof, and combinations thereof, for example. The adhesive composition may include from 0 to 90 percent by weight of the one or more tackifiers. More preferably, the adhesive composition includes 5 to 60 percent by weight of the one or more tackifiers, preferably 10 to 40 percent by weight, preferably 10 to 20 percent by weight.

In another aspect, the adhesive composition can include one or more waxes, such as polar waxes, non-polar waxes, Fischer-Tropsch waxes, oxidized Fischer-Tropsch waxes, hydroxystearamide waxes, functionalized waxes, polypropylene waxes, polyethylene waxes, wax modifiers, and combinations thereof, for example. The adhesive composition may include from 0 to 75 percent by weight the one or more waxes. More preferably, the adhesive composition includes 1 to 15 percent by weight of the one or more waxes.

In yet another aspect, the adhesive composition can include 60 percent by weight or less, 30 percent by weight or less, 20 percent by weight or less, 15 percent by weight or less, 10 percent by weight or less or 5 percent by weight or less of one or more additives. The one or more additives can include plasticizers, oils, stabilizers, antioxidants, pigments, dye-stuffs, antiblock additives, polymeric additives, defoamers, preservatives, thickeners, rheology modifiers, humectants, fillers, solvents, nucleating agents, surfactants, chelating agents, gelling agents, processing aids, cross-linking agents, neutralizing agents, flame retardants, fluorescing agents, compatibilizers, antimicrobial agents, and water, for example.

Exemplary oils may include aliphatic naphthenic oils, white oils, and combinations thereof, for example. The phthalates may include di-iso-undecyl phthalate (DIUP), di-isononylphthalate (DINP), dioctylphthalates (DOP), combinations thereof, or derivatives thereof. Exemplary polymeric additives include homo poly-alpha-olefins, copolymers of alpha-olefins, copolymers and terpolymers of diolefins, elastomers, polyesters, block copolymers including diblocks and triblocks, ester polymers, alkyl acrylate polymers, and acrylate polymers. Exemplary plasticizers may include mineral oils, polybutenes, phthalates, and combinations thereof.

Blends of Functionalized Polyolefins

In some embodiments, the polymers produced by this invention may be blended with of one or more other polymers, including but not limited to, thermoplastic polymer(s) and/or elastomer(s). Typically the bottlebrush polymer is present at from 0.1 wt % to 99 wt % (typically 1 wt % to 60 wt %, preferably 5 wt % to 40 wt %, and ideally about 10 wt % to about 45 wt %) based upon the weight of the blend and the other polymers are present at 99.9 wt % to 1 wt % (typically 99 wt % to 40 wt %, preferably 95 wt % to 60 wt %, preferably 90 wt % to 65 wt %).

By thermoplastic polymer(s), is meant a polymer that can be melted by heat and then cooled without appreciable change in properties. Thermoplastic polymers typically include, but are not limited to, polyolefins, polyamides, polyesters, polycarbonates, polysulfones, polyacetals, polyacetones, acrylonitrile-butadiene-styrene resins, polyphenylene oxide, polyphenylene sulfide, styrene-acrylonitrile resins, styrene maleic anhydride, polyimides, aromatic polyketones, or mixtures of two or more of the above. Preferred polyolefins include, but are not limited to, polymers comprising one or

more linear, branched or cyclic C_2 to C_{40} olefins, preferably polymers comprising propylene copolymerized with one or more C_3 to C_{40} olefins, preferably a C_3 to C_{20} alpha-olefin, more preferably C_3 to C_{10} alpha-olefins. More preferred polyolefins include, but are not limited to, polymers comprising ethylene including but not limited to ethylene copolymerized with a C_3 to C_{40} olefin, preferably a C_3 to C_{20} alpha-olefin, more preferably propylene and/or butene.

By elastomers, is meant all natural and synthetic rubbers, including those defined in ASTM D1566. Examples of preferred elastomers include, but are not limited to, ethylene propylene rubber, ethylene propylene diene monomer rubber, styrenic block copolymer rubbers (including SI, SIS, SB, SBS, SIBS, and the like, where S=styrene, I=isoprene, and B=butadiene), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, polybutadiene rubber (both cis and trans).

In another embodiment, the polymers produced herein may further be combined with one or more of polybutene, ethylene vinyl acetate, low density polyethylene (density 0.915 to less than 0.935 g/cm³) linear low density polyethylene, ultra-low density polyethylene (density 0.86 to less than 0.90 g/cm³), very low density polyethylene (density 0.90 to less than 0.915 g/cm³), medium density polyethylene (density 0.935 to less than 0.945 g/cm³), high density polyethylene (density 0.945 to 0.98 g/cm³), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, crosslinked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols and/or polyisobutylene. Preferred polymers include those available from ExxonMobil Chemical Company in Baytown, Tex. under the tradenames EXCEED™ and EXACT™.

Tackifiers may be blended with the polymers produced herein and/or with blends of the polymers produced by this invention (as described above). Examples of useful tackifiers include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and hydrogenated rosin esters. In some embodiments the tackifier is hydrogenated. In some embodiments the tackifier has a softening point (Ring and Ball, as measured by ASTM E-28) of 80° C. to 140° C., preferably 100° C. to 130° C. The tackifier, if present, is typically present at about 1 wt % to about 50 wt %, based upon the weight of the blend, more preferably 10 wt % to 40 wt %, even more preferably 20 wt % to 40 wt %.

In another embodiment, the functionalized (and optionally derivitized) polyolefins of this invention, and/or blends thereof, further comprise typical additives known in the art such as fillers, cavitating agents, antioxidants, surfactants, adjuvants, plasticizers, block, antiblock, color masterbatches,

pigments, dyes, processing aids, UV stabilizers, neutralizers, lubricants, waxes, and/or nucleating agents. The additives may be present in the typically effective amounts well known in the art, such as 0.001 wt % to 10 wt %. Preferred fillers, cavitating agents and/or nucleating agents include titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, talc, clay and the like. Preferred antioxidants include phenolic antioxidants, such as Irganox 1010, Irganox, 1076 both available from Ciba-Geigy. Preferred oils include paraffinic or naphthenic oils such as Primol 352, or Primol 876 available from ExxonMobil Chemical France, S. A. in Paris, France. More preferred oils include aliphatic naphthenic oils, white oils, or the like.

In a particularly preferred embodiment, the functionalized (and optionally derivitized) polyolefins produced herein are combined with polymers (elastomeric and/or thermoplastic) having functional groups such as unsaturated molecules-vinyl bonds, ketones or aldehydes under conditions such that they react. Reaction may be confirmed by an at least 20% (preferably at least 50%, preferably at least 100%) increase in Mw as compared to the Mw of the functionalized polyolefin prior to reaction. Such reaction conditions may be increased heat (for example, above the T_m of the functionalized polyolefin), increased shear (such as from a reactive extruder), presence or absence of solvent. Conditions useful for reaction include temperatures from 150° C. to 240° C. and where the components can be added to a stream comprising polymer and other species via a side arm extruder, gravimetric feeder, or liquids pump. Useful polymers having functional groups that can be reacted with the functionalized polyolefins produced herein include polyesters, polyvinyl acetates, nylons (polyamides), polybutadiene, nitrile rubber, hydroxylated nitrile rubber. In some embodiments, the functionalized (and optionally derivitized) polyolefin of this invention may be blended with up to 99 wt % (preferably up to 25 wt %, preferably up to 20 wt %, preferably up to 15 wt %, preferably up to 10 wt %, preferably up to 5 wt %), based upon the weight of the composition, of one or more additional polymers. Suitable polymers include:

PM1) Polyethylenes, including (but not limited to):

Copolymers of ethylene and one or more polar monomers, preferably selected from vinyl acetate, methyl acrylate, n-butyl acrylate, acrylic acid, and vinyl alcohol (i.e., EVA, EMA, EnBA, EAA, and EVOH); ethylene homopolymers and copolymers synthesized using a high-pressure free radical process, including LDPE; copolymers of ethylene and C₃ to C₄₀ olefins (preferably propylene and/or butene) with a density of greater than 0.91 g/cm³ to less than 0.94 g/cm³; including LLDPE; and high density PE (0.94 to 0.98 g/cm³).

PM2) Polybutene-1 and copolymers of polybutene-1 with ethylene and/or propylene.

PM3) Non-EP Rubber Elastomers, including (but not limited to):

Polyisobutylene, butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, and polybutadiene rubber (both cis and trans).

PM4) Low-crystallinity propylene/olefin copolymers, preferably random copolymers, comprising:

- i) at least 70 wt % propylene;
- ii) 5 wt % to 30 wt % (preferably 5 wt % to 20 wt %) of comonomer selected from ethylene and C₄ to C₁₂ olefins (preferably selected from ethylene, butene, and hexene; preferably ethylene);

preferably made using a metallocene-type catalyst; and having one or more of the following properties:

- a) Mw of 20 to 5,000 kg/mol (preferably 30 to 2,000 kg/mol, preferably 40 to 1,000 kg/mol, preferably 50 to 500 kg/mol, preferably 60 to 400 kg/mol); and/or
- b) molecular weight distribution index (Mw/Mn) of 1.5 to 10 (preferably 1.7 to 5, preferably 1.8 to 3); and/or
- c) GPC-determined g' index value of 0.9 or greater (preferably 0.95 or greater, preferably 0.99 or greater); and/or
- d) density of 0.85 to about 0.90 g/cm³ (preferably 0.855 to 0.89 g/cm³, preferably 0.86 to about 0.88 g/cm³); and/or
- e) melt flow rate (MFR) of at least 0.2 dg/min (preferably 1-500 dg/min, preferably 2-300 dg/min); and/or
- f) heat of fusion (Hf) of 0.5 J/g or more (preferably 1 J/g or more, preferably 2.5 J/g or more, preferably 5 J/g or more) but less than or equal to 75 J/g (preferably less than or equal to 50 J/g, preferably less than or equal to 35 J/g, preferably less than or equal to 25 J/g); and/or
- g) DSC-determined crystallinity of from 1 wt % to 30 wt % (preferably 2 wt % to 25 wt %, preferably 2 wt % to 20 wt %, preferably 3 wt % to 15 wt %); and/or
- h) a single broad melting transition with a peak melting point of 25° C. to about 105° C. (preferably 25° C. to 85° C., preferably 30° C. to 70° C., preferably 30° C. to 60° C.), where the highest peak considered the melting point; and/or
- i) crystallization temperature (T_c) of 90° C. or less (preferably 60° C. or less); and/or
- j) greater than 80% of the propylene residues (exclusive of any other monomer such as ethylene) arranged as 1,2 insertions with the same stereochemical orientation of the pendant methyl groups, either meso or racemic, as determined by ¹³C NMR; and/or
- k) ¹³C NMR-determined propylene tacticity index of more than 1; and/or
- l) ¹³C NMR-determined mm triad tacticity index of 75% or greater (preferably 80% or greater, preferably 82% or greater, preferably 85% or greater, preferably 90% or greater). Useful low-crystallinity propylene/olefin copolymers are available from ExxonMobil Chemical; suitable examples include Vistamaxx™ 6100, Vistamaxx™ 6200 and Vistamaxx™ 3000. Other useful low-crystallinity propylene/olefin copolymers are described in WO 03/040095, WO 03/040201, WO 03/040233, and WO 03/040442, all to Dow Chemical, which disclose propylene-ethylene copolymers made with non-metallocene catalyst compounds. Still other useful low-crystallinity propylene/olefin copolymers are described in U.S. Pat. No. 5,504,172 to Mitsui Petrochemical. Preferred low-crystallinity propylene/olefin copolymers are described in U.S. Published Application No. 2002/0004575 to ExxonMobil Chemical.

PM5) Propylene oligomers suitable for adhesive applications, such as those described in WO 2004/046214, particularly those at pages 8 to 23.

PM6) Olefin block copolymers, including those described in WO 2005/090425, WO 2005/090426, and WO 2005/090427.

PM7) Polyolefins that have been post-reactor functionalized with maleic anhydride (so-called maleated polyolefins),

including maleated ethylene polymers, maleated EP Rubbers, and maleated propylene polymers. Preferably, the amount of free acid groups present in the maleated polyolefin is less than about 1000 ppm (preferably less than about 500 ppm, preferably less than about 100 ppm), and the amount of phosphite present in the maleated polyolefin is less than 100 ppm.

PM8) Styrenic Block Copolymers (SBCs), including (but not limited to):

Unhydrogenated SBCs such as SI, SIS, SB, SBS, SIBS and the like, where S=styrene, I=isobutylene, and B=butadiene; and hydrogenated SBCs, such as SEBS, where EB=ethylene/butene.

PM9) Engineering Thermoplastics, including (but are not limited to):

Polycarbonates, such as poly(bisphenol-a carbonate); polyamide resins, such as nylon 6 (N6), nylon 66 (N66), nylon 46 (N46), nylon 11 (N11), nylon 12 (N12), nylon 610 (N610), nylon 612 (N612), nylon 6/66 copolymer (N6/66), nylon 6/66/610 (N6/66/610), nylon MXD6 (MXD6), nylon 6T (N6T), nylon 6/6T copolymer, nylon 66/PP copolymer, and nylon 66/PPS copolymer; polyester resins, such as polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyethylene isophthalate (PEI), PET/PEI copolymer, polyacrylate (PAR), polybutylene naphthalate (PBN), liquid crystal polyester, polyoxalkylene diimide diacid/polybutyrate terephthalate copolymer, and other aromatic polyesters; nitrile resins, such as polyacrylonitrile (PAN), polymethacrylonitrile, styrene-acrylonitrile copolymers (SAN), methacrylonitrile-styrene copolymers, and methacrylonitrile-styrene-butadiene copolymers; acrylate resins, such as polymethyl methacrylate and polyethylacrylate; polyvinyl acetate (PVAc); polyvinyl alcohol (PVA); chloride resins, such as polyvinylidene chloride (PVDC), and polyvinyl chloride (PVC); fluoride resins, such as polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), polychlorofluoroethylene (PCFE), and polytetrafluoroethylene (PTFE); cellulose resins, such as cellulose acetate and cellulose acetate butyrate; polyimide resins, including aromatic polyimides; polysulfones; polyacetals; polylactones; polyketones, including aromatic polyketones; polyphenylene oxide; polyphenylene sulfide; styrene resins, including polystyrene, styrene-maleic anhydride copolymers, and acrylonitrile-butadiene-styrene resin.

PM10) EP Rubbers, including copolymers of ethylene and propylene, and optionally one or more diene monomer(s), where the ethylene content is from 35 mol % to 85 mol %, the total diene content is 0 mol % to 5 mol %, and the balance is propylene with a minimum propylene content of 15 mol %. Typically, the EP Rubbers have a density of less than 0.86 g/cc.

Polymer Products

The polymer products produced herein typically have a weight average molecular weight (as measured by GPC) of at least 1000 g/mol, preferably at least 5,000 g/mol, preferably at least 10,000 g/mol, preferably at least 20,000 g/mol, preferably at least 30,000 g/mol and preferably have an Mw (GPC) of less than 2,000,000 g/mol, preferably less than 1,000,000 g/mol, preferably less than 500,000 g/mol.

Applications

The polymers of this invention (and blends thereof as described above) may be used in any known thermoplastic or elastomer application. Examples include uses in molded parts, films, tapes, sheets, tubing, hose, sheeting, wire and cable coating, adhesives, shoe soles, bumpers, gaskets, bel-

lows, films, fibers, elastic fibers, nonwovens, spun bonds, corrosion protection coatings and sealants. The functionalized polymers of the invention can also be used as protective films, such as those described in U.S. Pat. No. 7,323,239 and also as rosin tackifiers and as heat sealable films such as those described in U.S. Pat. No. 4,921,749, the contents of which are incorporated herein in their entirety for all purposes.

In another embodiment the polymers can be used as a compatibilizer for particulate materials, such as carbon black, silica, glass, etc. or other high surface tension materials when the material is being blended into another polymer (such as polystyrene, polyethylene, polypropylene, butyl rubber, SBR, natural rubber, and other polymers named as PM1 to PM10 above).

EXAMPLES

Product Characterization

Products were characterized by ^1H NMR and ^{13}C NMR as follows:

^1H NMR

Unless otherwise stated, ^1H NMR data was collected at either room temperature or 120° C. in a 5 mm probe using a spectrometer with a ^1H frequency of at least 400 MHz. Data was recorded using a maximum pulse width of 45°, 8 seconds between pulses and signal averaging 32 transients. Samples were dissolved in benzene- d_6 or toluene- d_8 at concentrations between 5 to 40 wt % prior to insertion in the spectrometer magnet. Prior to data analysis spectra were referenced by setting the chemical shift of the benzene solvent signal to 7.15 ppm or the least shifted toluene solvent signal to 2.08 ppm.

^{13}C NMR

Unless otherwise stated, ^{13}C NMR data was collected at room temperature using a spectrometer with a ^{13}C frequency of at least 100 MHz. A 90 degree pulse, an acquisition time adjusted to give a digital resolution between 0.1 and 0.12 Hz, at least a 10 second pulse acquisition delay time with continuous broadband proton decoupling using swept square wave modulation without gating was employed during the entire acquisition period. Samples were dissolved in benzene- d_6 or chloroform- d at concentrations between 10 to 40 wt % prior to being inserted into the spectrometer magnet.

Prior to data analysis spectra were referenced by setting the chemical shift of the benzene solvent signal to 128.06 ppm or the chloroform solvent signal to 77.16 ppm.

Gel Permeation Chromatography (GPC)

Mw, Mn and Mw/Mn are determined by using a High Temperature Gel Permeation Chromatograph (Polymer Laboratories), equipped with three in-line detectors (3D), a differential refractive index detector (DRI), a light scattering (LS) detector, and a viscometer. Experimental details, including detector calibration, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001) and references therein. Three Polymer Laboratories PLgel 10 μm Mixed-B LS columns are used. The nominal flow rate is 0.5 ml/min, and the nominal injection volume is 300 μL . The various transfer lines, columns, viscometer and differential refractometer (the DRI detector) are contained in an oven maintained at 145° C. Solvent for the experiment is prepared by dissolving 6 grams of butylated hydroxytoluene as an antioxidant in 4 liters of Aldrich reagent grade 1,2, 4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.1 μm Teflon filter. The TCB is then degassed with an online degasser before entering the Size Exclusion Chromatograph. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating

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the mixture at 160° C. with continuous shaking for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature and 1.284 g/ml at 145° C. The injection concentration is from 0.5 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector and the injector are purged. Flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8 to 9 hours before injecting the first sample. The LS laser is turned on at least 1 to 1.5 hours before running the samples. The concentration, *c*, at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, *I*_{DRI}, using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc)$$

where *K*_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, *n*=1.500 for TCB at 145° C. and λ=690 nm. (dn/dc) is determined by GPC-DRI. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g.

The LS detector is a Wyatt Technology High Temperature DAWN HELEOS. The molecular weight, *M*, at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M. B. Hugglin, LIGHT SCATTERING FROM POLYMER SOLUTIONS, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c$$

Here, Δ*R*(θ) is the measured excess Rayleigh scattering intensity at scattering angle θ, *c* is the polymer concentration determined from the DRI analysis, *A*₂ is the second virial coefficient, and for purposes of this invention *A*₂=0.0006. *P*(θ) is the form factor for a monodisperse random coil, and *K*_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where *N*_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system determined by GPC-DRI. The refractive index, *n*=1.500 for TCB at 145° C. and λ=657 nm.

A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s, for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, [η], at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where *c* is concentration and was determined from the DRI output.

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The branching index (*g'*_{vis}) is calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity, *H*_{avg}, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, *i*, between the integration limits. The branching index *g'*_{vis} is defined as:

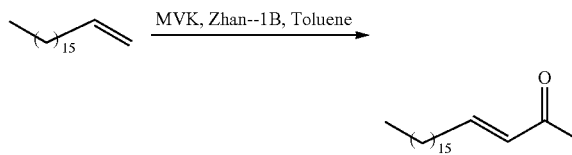
$$g'_{vis} = \frac{[\eta]_{avg}}{k M_v^\alpha}$$

where, for purpose of this invention and claims thereto, α=0.705 *k*=0.0002288. *M*_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. See Macromolecules, 2001,34, pp. 6812-6820 and Macromolecules, 2005, 38, pp. 7181-7183, for guidance on selecting a linear standard having similar molecular weight and comonomer content, and determining *k* coefficients and α exponents. *Z* average branching index (*g'*_{Zave}) is calculated using *C*_i=polymer concentration in the slice *i* in the polymer peak times the mass of the slice squared, *M*_i².

All molecular weights are weight average unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted.

The ruthenium catalyst employed in examples below (referred to as "Zhan 1B") is 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(*i*-propoxy)-5-(*N,N*-dimethylaminosulfonylphenyl)methyl]ruthenium(II) dichloride (CAS Number: 918870-76-5)

Example 1.

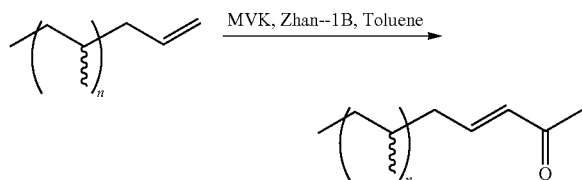


In a nitrogen-filled glovebox, a 100 mL round bottom flask at room temperature was charged with 1-octadecene (3.21 mL, 10.1 mmol), 3-buten-2-one (MVK) (3.53 mL, 50.3 mmol), toluene (50 mL), and a magnetic stirbar. The solution was stirred and heated to 50° C. Zhan-1B catalyst (38 mg, 0.5 mol) was then added as a solution in toluene (1 mL) and vigorous gas evolution was observed. The flask was loosely capped and allowed to stir at 50° C. for 16 h. The mixture was concentrated under a constant flow of nitrogen yielding an off-white solid. The resulting solid was dissolved in pentane and filtered through a plug of layered celite/silica/celite, leav-

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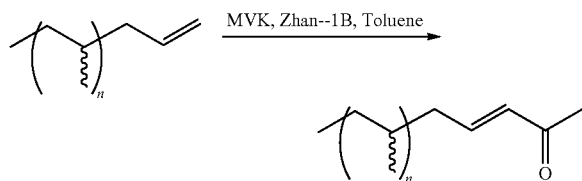
ing a colorless filtrate. This solution was concentrated under reduced pressure yielding a white solid. (2.50 g, 85%)

Example 2.



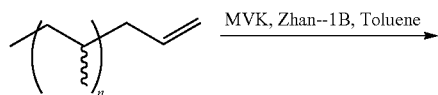
In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with vinyl terminated atactic homopolypropylene (aPP) (936 mg, 1.63 mmol, Mn=571, vinyl=98%, based on total unsaturations), 3-buten-2-one (MVK) (0.66 mL, 8.2 mmol), toluene (15.3 mL), and a magnetic stirbar. The solution was stirred and heated to 60° C. Zhan-1B catalyst (12.4 mg, 0.016 mmol) was then added as a solution in toluene (1 mL) and vigorous gas evolution was observed. The vial was loosely capped and allowed to stir at 60° C. for 16 h. The mixture was concentrated under a constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite, leaving a colorless filtrate. This solution was concentrated under reduced pressure yielding a colorless oil. (834 mg, 83%)

Example 3.



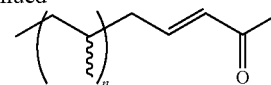
In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with vinyl terminated aPP (885 mg, 0.26 mmol, Mn=3571, vinyl=95%, based on total unsaturations), 3-buten-2-one (MVK) (0.63 mL, 7.8 mmol), toluene (15.5 mL), and a magnetic stirbar. The solution was stirred and heated to 60° C. Zhan-1B catalyst (12 mg, 0.015 mmol) was then added as a solution in toluene (1 mL) and vigorous gas evolution was observed. The vial was loosely capped and allowed to stir at 60° C. for 16 h. The mixture was concentrated under a constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite, leaving a colorless filtrate. This solution was concentrated under reduced pressure yielding a colorless oil. (829 mg, 93%)

Example 4.



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In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with vinyl terminated aPP (3.1 g, 0.20 mmol, Mn=14,894, vinyl=71%, based on total unsaturations), 3-buten-2-one (MVK) (0.99 mL, 12.2 mmol), toluene (15 mL), and a magnetic stirbar. The solution was stirred and heated to 60° C. Zhan-1B catalyst (18 mg, 0.025 mmol) was then added as a solution in toluene (1 mL) and vigorous gas evolution was observed. The vial was loosely capped and allowed to stir at 60° C. for 16 h. The mixture was concentrated under a constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite, leaving a colorless filtrate. This solution was concentrated under reduced pressure yielding a colorless oil. (2.2 g, 71%)

Example 5.

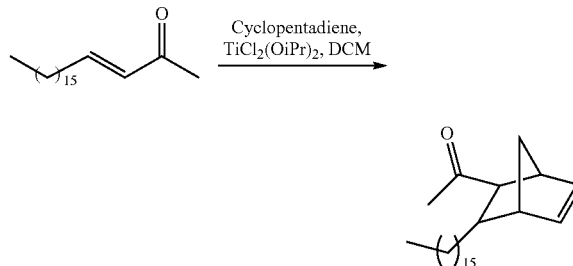
1-(3-hexadecylbicyclo[2.2.1]hept-5-en-2-yl)ethanone.

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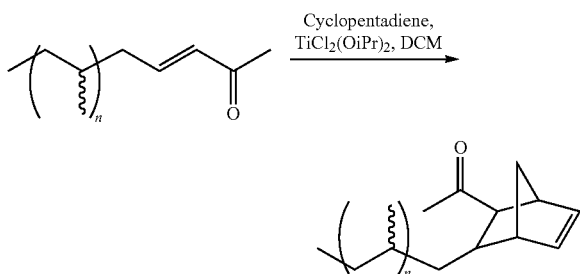
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In a nitrogen-filled glovebox, a 50 mL round bottom flask at room temperature was charged with 3-eicosen-2-one (1.216 g, 4.12 mmol), cyclopentadiene (954 mg, 10.3 mmol), dichloromethane (15 mL), and a magnetic stirbar. The mixture was stirred, and diisopropoxytitanium(IV) chloride (48 mg, 0.2 mmol) was added as a solid. The flask was capped and allowed to stir for 36 h at room temperature. The flask was removed from the glovebox and water (2 mL) was added and the mixture was allowed to stir for 30 minutes. Stirring was stopped and the resulting biphasic mixture was allowed to stand and separate. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (DCM) (3×10 mL). The combined organic solution was dried with MgSO₄, filtered, and concentrated under a constant flow of nitrogen. The residue was further concentrated in a vacuum oven for 3 days at 60° C. yielding a colorless oil (1.231 g, 83%). ¹H NMR (400 MHz, C₆D₆) δ 6.1 (dd, 1H, J=5.7, 3.1), 5.8 (dd, 1H, J=5.7, 2.8), 2.8 (m, 1H), 2.4 (m, 1H), 2.0 (dd, 1H, J=4.4, 3.5), 1.9 (m, 1H), 1.7 (bs, 2H), 1.4-1.2 (m, 30H), 0.9 (t, 3H, J=13.7).

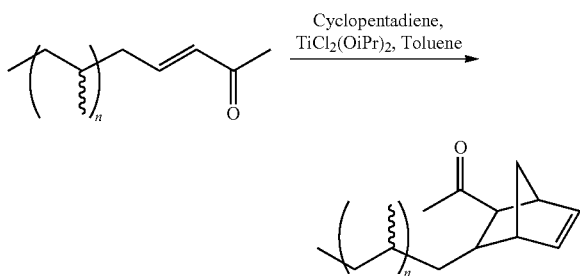
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Example 6.



In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with enone-terminated aPP from Example 2 (628 mg, 1.02 mmol), cyclopentadiene (196 mg, 2.04 mmol), dichloromethane (10 mL), and a magnetic stirbar. The mixture was stirred, and diisopropoxytitanium (IV) chloride (24 mg, 0.1 mmol) was added as a solid. The flask was capped and allowed to stir for 36 h at room temperature. The flask was removed from the glovebox and water (2 mL) was added and the mixture was allowed to stir for 30 minutes. Stirring was stopped and the resulting biphasic mixture was allowed to stand and separate. The organic layer was separated, and the aqueous layer was extracted with DCM (3×5 mL). The combined organic solution was dried with MgSO₄, filtered, and concentrated under a constant flow of nitrogen. The residue was further concentrated in a vacuum oven for 3 days at 60° C. yielding a colorless oil (578 mg, 83%). ¹H NMR (400 MHz, C₆D₆) δ 6.1 (d, 1H, J=12.6), 5.8 (d, 1 H, J=22.8), 2.8 (bs, 1H), 2.4 (bs, 1H), 2.3-2.0 (m, 2H), 1.8-0.8 (m, 80H).

Example 7.

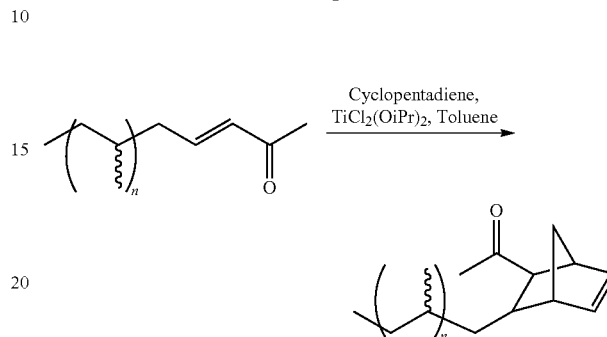


In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with enone-terminated aPP from Example 3 (310 mg, 0.08 mmol), cyclopentadiene (40 mg, 0.43 mmol), toluene (10 mL), and a magnetic stirbar. The mixture was stirred, and diisopropoxytitanium(IV) chloride (2 mg, 8×10⁻³ mmol) was added as a solid. The flask was capped and allowed to stir for 36 h at room temperature. The flask was removed from the glovebox and water (2 mL) was added and the mixture was allowed to stir for 30 minutes. Stirring was stopped and the resulting biphasic mixture was allowed to stand and separate. The organic layer was separated, and the aqueous layer was extracted with toluene (3×5

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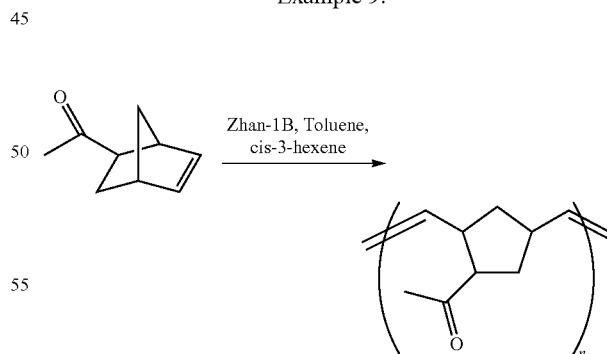
mL). The combined organic solution was dried with MgSO₄, filtered, and concentrated under a constant flow of nitrogen. The residue was further concentrated in a vacuum oven for 3 days at 60° C. yielding a colorless oil (227 mg, 72%). ¹H NMR (400 MHz, C₆D₆) δ 6.1 (d, 1H, J=17.3), 5.8 (d, 1 H, J=24.8), 2.8 (bs, 1H), 2.4 (m, 1H), 2.2-2.1 (m, 3H), 1.8-0.8 (m, 480H).

Example 8.



In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with enone terminated aPP from Example 4 (700 mg, 0.046 mmol), cyclopentadiene (16 mg, 0.175 mmol), toluene (10 mL), and a magnetic stirbar. The mixture was stirred, and diisopropoxytitanium(IV) chloride (1 mg, 4×10⁻³ mmol) was added as a solid. The flask was capped and allowed to stir for 36 h at room temperature. The flask was removed from the glovebox and water (2 mL) was added and the mixture was allowed to stir for 30 minutes. Stirring was stopped and the resulting biphasic mixture was allowed to stand and separate. The organic layer was separated, and the aqueous layer was extracted with toluene (3×5 mL). The combined organic solution was dried with MgSO₄, filtered, and concentrated under a constant flow of nitrogen. The residue was further concentrated in a vacuum oven for 3 days at 60° C. yielding a colorless oil (663 mg, 95%). ¹H NMR (400 MHz, C₆D₆) δ 6.1 (d, 1H, J=17.3), 5.8 (d, 1 H, J=24.6), 2.8 (bs, 1H), 2.4 (m, 1H), 1.9-1.5 (m, 1000H), 1.5-0.8 (m, 1800H), 0.4 (bs, 3H).

Example 9.

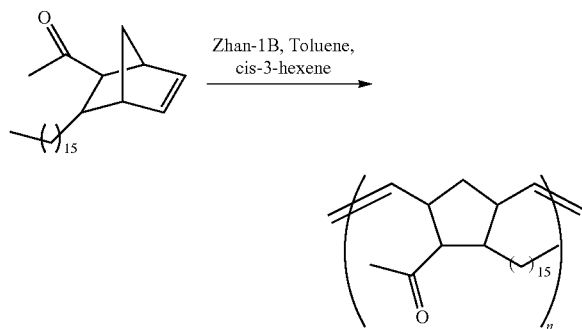


In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with 2-acetyl-5-norbornene (471 mg, 3.5 mmol), cis-3-hexene (14.5 mg, 0.17 mmol), toluene (17 mL), and a magnetic stirbar. The solution was stirred, and Zhan-1B catalyst (13 mg, 0.017 mmol) was added as a solution in toluene (1 mL). The flask was loosely capped and allowed to stir for 16 h. The mixture was concentrated under constant flow of nitrogen yielding an orange oil. The

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resulting oil was immiscible in pentane, redissolved in toluene and filtered through a plug of layered celite/silica/celite. This solution was concentrated to approximately 0.5 mL under reduced pressure and then 20 mL of methanol were added while the solution was stirred. The suspension was allowed to stand and settle for 4 days and the liquid was then decanted. The solid was redissolved in toluene and filtered again through a plug of layered celite/silica/celite. The filtrate was then concentrated, yielding a light tan oil. (98 mg, 21%)

Example 10.

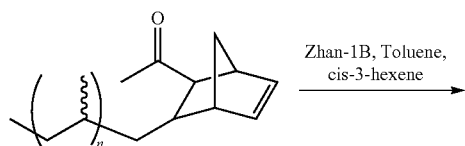


In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with 1-(3-hexadecylbicyclo [2.2.1]hept-5-en-2-yl)ethanone (1.231 g, 3.4 mmol), cis-3-hexene (21 μ L, 0.17 mmol), toluene (18 mL), and a magnetic stirbar. The solution was stirred, and Zhan-1B catalyst (20 mg, 0.017 mmol) was added as a solution in toluene (1 mL). The flask was loosely capped and allowed to stir for 16 h. The mixture was concentrated under constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered twice through plugs of layered celite/silica/celite. This solution was concentrated under reduced pressure yielding a yellow oil (1.02 g, 82%). ^1H NMR (400 MHz, C_6D_6) δ 5.4 (br, 2H), 3.2 (br, 1H), 2.8 (br, 1H), 2.6 (br, 1H), 2.4 (br, 1H), 2.1 (br, 2H), 2.0 (br, 2H), 1.6 (br, 2H), 1.4 (br, 31H), 0.9 (br, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 67.1, 32.2, 30.1, 29.7, 23.0, 14.2 (carbonyl not observed due to low signal to noise ratio).

FIG. 1 provides intrinsic viscosity versus molecular weight of Example 10 product measured by MALLS/3D analysis.

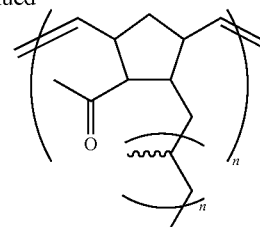
Example 11.

ROMP of the Product of Example 6.



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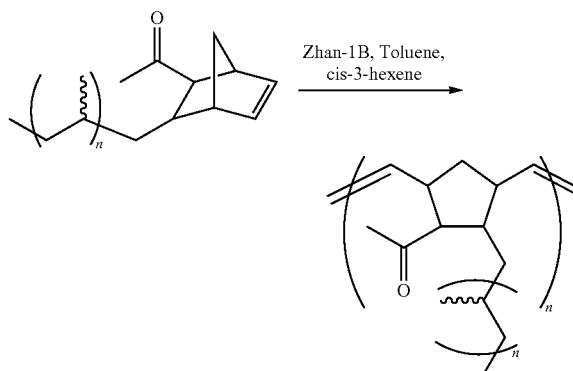


In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with the product of Example 6 (578 mg, 0.85 mmol), cis-3-hexene (5.3 μ L, 0.04 mmol), toluene (10 mL), and a magnetic stirbar. The solution was stirred, and Zhan-1B catalyst (6.4 mg, 8×10^{-3} mmol) was added as a solution in toluene (1 mL). The flask was loosely capped and allowed to stir for 16 h. The mixture was concentrated under constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite. This solution was concentrated under reduced pressure. The residue was further concentrated in a vacuum oven for 6 h at 60° C. yielding a yellow oil (344 mg, 60%). ^1H NMR (400 MHz, C_6D_6) δ 5.4 (br, 2H), 3.3 (br, 1H), 2.9 (br, 1H), 2.6 (br, 2H), 2.2 (br), 1.8 (br), 1.5-0.8 (br); ^{13}C NMR (125 MHz, C_6D_6) δ 66.5, 47.4, 46.9, 32.0, 27.9, 25.6, 23.6, 23.0, 20.6, 14.3 (carbonyl not observed due to low signal to noise ratio).

FIG. 2 provides intrinsic viscosity versus molecular weight of Example 11 product measured by MALLS/3D analysis.

Example 12.

ROMP of the Product of Example 7.



In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with the product of Example 7 (227 mg, 0.062 mmol), cis-3-hexene (0.4 μ L, 0.003 mmol), toluene (10 mL), and a magnetic stirbar. The solution was stirred, and Zhan-1B catalyst (0.47 mg, 6×10^{-4} mmol) was added as a solution in toluene (1 mL). The flask was loosely capped and allowed to stir for 16 h. The mixture was concentrated under constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite. This solution was concentrated under reduced pressure. The residue was further concentrated in a vacuum oven for 6 h at 60° C. yielding a yellow oil (161 mg, 71%). ^1H NMR (400 MHz, C_6D_6) δ 5.5 (br, 2H), 3.3 (br, 1H), 2.8 (br, 1H), 2.6 (br, 2H),

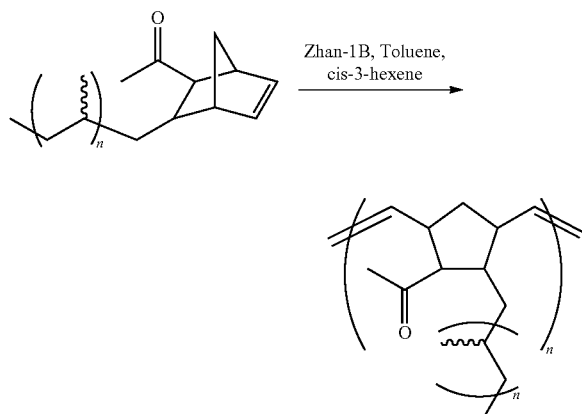
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2.2 (br), 1.8 (br), 1.5-0.8 (br); ^{13}C NMR (125 MHz, C_6D_6) δ 47.1, 46.3, 46.1, 45.6, 44.5, 44.3, 27.8, 27.4, 25.2, 21.5, 21.1, 20.7, 20.3, 19.6, 14.2 (carbonyl not observed due to low signal to noise ratio).

FIG. 3 provides intrinsic viscosity versus molecular weight of Example 12 product measured by MALLS/3D analysis.

Example 13.

ROMP of the Product of Example 8.



In a nitrogen-filled glovebox, a 20 mL scintillation vial at room temperature was charged with the product of Example 8 (663 mg, 0.033 mmol), cis-3-hexene (0.2 μL , 0.002 mmol), toluene (10 mL), and a magnetic stirbar. The solution was stirred, and Zhan-1B catalyst (0.25 mg, 3×10^{-4} mmol) was added as a solution in toluene (1 mL). The flask was loosely capped and allowed to stir for 16 h. The mixture was concentrated under constant flow of nitrogen yielding an orange oil. The resulting oil was dissolved in pentane and filtered through a plug of layered celite/silica/celite. This solution was concentrated under reduced pressure. The residue was further concentrated in a vacuum oven for 6 h at 60° C. yielding a yellow oil (545 mg, 82%). ^1H NMR (400 MHz, C_6D_6) δ 5.5 (br), 2.2 (br), 1.8 (br), 1.5-0.8 (br).

FIG. 4 provides intrinsic viscosity versus molecular weight of Example 13 product measured by MALLS/3D analysis.

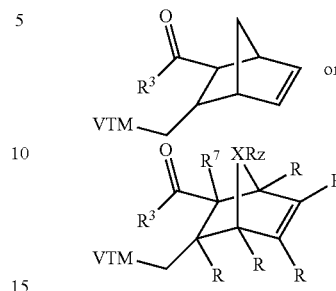
Example	dn/dc	M_n (GPC-)	M_w (GPC)	$g'(\text{vis})$
10	0.0575	17,882	28,916	0.356
11	0.0819	16,650	35,573	0.309
12	0.0998	45,114	89,671	0.393
13	0.1029	64,644	215,178	0.53

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text, provided however that any priority document not named in the initially filed application or filing documents is NOT incorporated by reference herein.

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The invention claimed is:

1. A composition represented by the formula:



where VTM is the residual terminal portion of a vinyl terminated macromonomer and R^3 is a C_1 to a C_{40} hydrocarbyl group, each R is, independently, H or a C_1 to C_{40} hydrocarbyl group and R^7 is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl, X is C or a heteroatom, and z is 0 or 1.

2. The composition of claim 1, wherein the residual portion of the vinyl terminated macromonomer is derived from 1-octadecene.

3. The composition of claim 1, wherein the VTM is one or more of:

- (i) a vinyl terminated polymer having at least 5% allyl chain ends;
- (ii) a vinyl terminated polymer having an M_n at least 160 g/mol (measured by ^1H NMR) comprising of one or more C_4 to C_{40} higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and

wherein the higher olefin polymer has at least 5% allyl chain ends;

- (iii) a copolymer having an M_n of 300 g/mol or more (measured by ^1H NMR) comprising (a) from about 20 mol% to about 99.9 mol% of at least one C_5 to C_{40} higher olefin, and (b) from about 0.1 mol% to about 80 mol% of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends;

- (iv) a copolymer having an M_n of 300 g/mol or more (measured by ^1H NMR), and comprises (a) from about 80 mol% to about 99.9 mol% of at least one C_4 olefin, (b) from about 0.1 mol% to about 20 mol% of propylene; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;

- (v) a co-oligomer having an M_n of 300 g/mol to 30,000 g/mol (measured by ^1H NMR) comprising 10 mol% to 90 mol% propylene and 10 mol% to 90 mol% of ethylene, wherein the oligomer has at least X% allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 * (\text{mol}\% \text{ ethylene incorporated}) + 100)$, when 10 mol% to 60 mol% ethylene is present in the co-oligomer, 2) $X = 45$, when greater than 60 mol% and less than 70 mol% ethylene is present in the co-oligomer, and 3) $X = (1.83 * (\text{mol}\% \text{ ethylene incorporated}) - 83)$, when 70 mol% to 90 mol% ethylene is present in the co-oligomer;

- (vi) a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the oligomer has: at least 93% allyl chain ends, a number average molecular weight (M_n) of about 500 g/mol to about 20,000 g/mol, an isobutyl chain end to allylic vinyl

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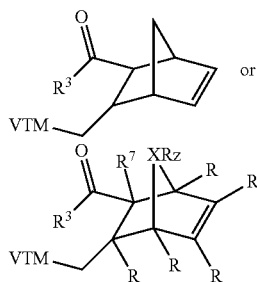
group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units;

- (vii) a propylene oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 20,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;
- (viii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C₄ to C₁₂ olefin, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0;
- (ix) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
- (x) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, an Mn of about 500 g/mol to about 70,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
- (xi) vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.06; (c) a $g'_{(vis)}$ of greater than 0.95; and (d) an Mn (¹H NMR) of at least 20,000 g/mol; and
- (xii) vinyl terminated polyethylene having: (a) at least 50% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of 0.95 or less; (d) an Mn (¹H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (¹H NMR) in the range of from about 0.8 to about 1.2.

4. A process to prepare the composition of claim 1, comprising the step of contacting a cyclopentadiene with a titanium catalyst and an enone terminated VTM.

5. The process of claim 4, wherein the cyclopentadiene is substituted at one or more positions.

6. A composition comprising the reaction product of: a C3 to a C40 vinyl or vinyne containing monomer, a ruthenium catalyst and a composition represented by the formula:



where VTM is the residual terminal portion of a vinyl terminated macromonomer and R³ is a C1 to a C40 hydrocarbyl group, each R is, independently, H or a C1 to C40 hydrocarbyl group, R⁷ is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl, X is C or a heteroatom, and z is 0 or 1.

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7. The composition of claim 6, wherein the residual portion of the vinyl terminated macromonomer is derived from 1-octadecene.

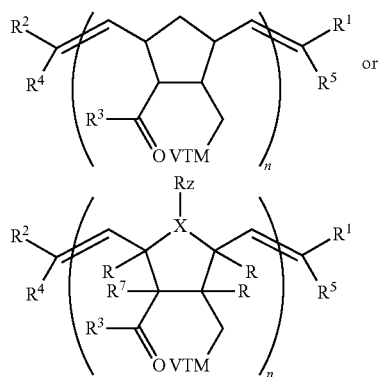
8. The composition of claim 6, wherein the VTM is one or more of:

- (i) a vinyl terminated polymer having at least 5% allyl chain ends;
- (ii) a vinyl terminated polymer having an Mn at least 160 g/mol (measured by ¹H NMR) comprising of one or more C₄ to C₄₀ higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends;
- (iii) a copolymer having an Mn of 300 g/mol or more (measured by ¹H NMR) comprising (a) from about 20 mol% to about 99.9 mol% of at least one C₅ to C₄₀ higher olefin, and (b) from about 0.1 mol% to about 80 mol% of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends;
- (iv) a copolymer having an Mn of 300 g/mol or more (measured by ¹H NMR), and comprises (a) from about 80 mol% to about 99.9 mol% of at least one C₄ olefin, (b) from about 0.1 mol% to about 20 mol% of propylene; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;
- (v) a co-oligomer having an Mn of 300 g/mol to 30,000 g/mol (measured by ¹H NMR) comprising 10 mol% to 90 mol% propylene and 10 mol% to 90 mol% of ethylene, wherein the oligomer has at least X% allyl chain ends (relative to total unsaturations), where: 1) X = (-0.94*(mol% ethylene incorporated) + 100), when 10 mol% to 60 mol% ethylene is present in the co-oligomer, 2) X = 45, when greater than 60 mol% and less than 70 mol% ethylene is present in the co-oligomer, and 3) X = (1.83*(mol% ethylene incorporated) - 83), when 70 mol% to 90 mol% ethylene is present in the co-oligomer;
- (vi) a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the oligomer has: at least 93% allyl chain ends, a number average molecular weight (Mn) of about 500 g/mol to about 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units;
- (vii) a propylene oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 20,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;
- (viii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C₄ to C₁₂ olefin, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0;
- (ix) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
- (x) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, an Mn of about 500 g/mol to about 70,000 g/mol, an isobutyl

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- chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
- (xi) vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of greater than 0.95; and (d) an Mn (^1H NMR) of at least 20,000 g/mol; and
- (xii) vinyl terminated polyethylene having: (a) at least 50% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of 0.95 or less; (d) an Mn (^1H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (^1H NMR) in the range of from about 0.8 to about 1.2.

9. The composition of claim 6 represented by the formula:



wherein VTM is the residual terminal portion of a vinyl terminated macromonomer;

each R^1 , R^2 , R^4 and R^5 , is independently, a C2 to C40 hydrocarbyl group;

R^3 is a C1 to a C40 hydrocarbyl group;

each R is, independently, H or a C1 to C40 hydrocarbyl group;

R^7 is a substituted or unsubstituted alkyl or substituted or unsubstituted aryl,

X is C or a heteroatom;

z is 0 or 1; and

n is from 2 to about 2000.

10. The composition of claim 9, wherein the residual portion of the vinyl terminated macromonomer is derived from 1-octadecene.

11. The composition of claim 6, wherein the VTM comprises a vinyl terminated polymer having at least 5% allyl chain ends.

12. The composition of claim 6, wherein the VTM comprises a vinyl terminated polymer having an Mn at least 160 g/mol (measured by ^1H NMR) comprising of one or more C_4 to C_{40} higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends.

13. The composition of claim 6, wherein the VTM comprises a copolymer having an Mn of 300 g/mol or more

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(measured by ^1H NMR) comprising (a) from about 20 mol% to about 99.9 mol% of at least one C_5 to C_{40} higher olefin, and (b) from about 0.1 mol% to about 80 mol% of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends.

14. The composition of claim 6, wherein the VTM comprises a copolymer having an Mn of 300 g/mol or more (measured by ^1H NMR), and comprises (a) from about 80 mol% to about 99.9 mol% of at least one C_4 olefin, (b) from about 0.1 mol% to about 20 mol% of propylene; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation.

15. The composition of claim 6, wherein the VTM comprises a co-oligomer having an Mn of 300 g/mol to 30,000 g/mol (measured by ^1H NMR) comprising 10 mol% to 90 mol% propylene and 10 mol% to 90 mol% of ethylene, wherein the oligomer has at least X% allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 * (\text{mol\% ethylene incorporated}) + 100)$, when 10 mol% to 60 mol% ethylene is present in the co-oligomer, 2) $X = 45$, when greater than 60 mol% and less than 70 mol% ethylene is present in the co-oligomer, and 3) $X = (1.83 * (\text{mol\% ethylene incorporated}) - 83)$, when 70 mol% to 90 mol% ethylene is present in the co-oligomer.

16. The composition of claim 6, wherein the VTM comprises a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the oligomer has: at least 93% allyl chain ends, a number average molecular weight (Mn) of about 500 g/mol to about 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units.

17. The composition of claim 6, wherein the VTM comprises a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C_4 to C_{12} olefin, wherein the oligomer has: at least 90% allyl chain ends, an Mn of about 150 g/mol to about 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0.

18. The composition of claim 6, wherein the VTM comprises a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, an Mn of about 500 g/mol to about 70,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum.

19. The composition of claim 6, wherein the VTM comprises a vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of greater than 0.95; and (d) an Mn (^1H NMR) of at least 20,000 g/mol.

20. The composition of claim 6, wherein the VTM comprises a vinyl terminated polyethylene having: (a) at least 50% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of 0.95 or less; (d) an Mn (^1H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (^1H NMR) in the range of from about 0.8 to about 1.2.

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